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What does the future hold for polyurethane fashion and design?

Conservation studies regarding the 1960s and 1970s objects from the MUDE collection

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What does the future hold for polyurethane fashion and design? Conservation studies regarding the 1960s and 1970s objects from the MUDE collection

Dedicated to my lucky star

Avô António Manuel

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Abstract

Polyurethane (PUR) is one of the most difficult synthetic polymers to preserve. The main aim of this research is to assist PUR condition assessment on historical objects and define storage conditions for this perishable material (20–50 years). According to the current knowledge, PUR continues to degrade even if exposed to controlled conditions (18–21°C, ≈50% RH, in the dark) and following PUR degradation, damage is irreversible. PUR degradation forms include yellowing, crumbling, brittleness and/or chalking, among others.

Twenty-four selected PUR-based design and fashion objects (1960s–1970s) from *MUDE – Museu do Design e da Moda, Coleção Francisco Capelo* (Lisbon) were studied using optical microscopy (visible, UV light) and infrared and Raman microspectroscopies. In this thesis, national and international case studies have been included: foams (ether- and ester based), films (ester-based) and fibres (ether-based); showing fair, poor and unacceptable conditions. Unaged (good condition) and naturally pre-aged references were studied by submitting to natural (outdoor) and artificial (λ>300 nm) ageing experiments. Based on this approach, different PUR degradation stages are analysed, and visual (micro level) and molecular pathways for PUR natural ageing are suggested. PUR deterioration signs are translated into specific infrared fingerprints (assigned to N–H, C–H and C=O stretching absorptions), and the band at c. 1640 cm^{-1} ($C{=}O_{urea}$ stretching) is proposed as an IR marker for PUR condition assessment. PUR H-bonds (PUR physical crosslinking) are confirmed as liable to natural ageing conditions. To plan a preventive strategy for PUR, a natural ageing experiment (12 months in darkness, 45–55% RH) was carried out for four storage conditions: open air at room T; sealed enclosures at room T, with/without oxygen and at low T (11–13°C). Samples were analysed by colourimetry, gravimetry, contact angle, hardness, optical microscopy, and infrared and Raman microspectroscopies. Further statistical data treatment (ANOVA) was carried out to identify significant variations and to uncover correlations between molecular spectral lines and physical aspects. Raman proved to be a powerful tool in the detection of early stage PUR molecular deterioration and sensitive to molecular changes responsible for yellowing increase. Open-air storage proved to be the most harmful condition, whereas anoxic storage showed the best results. Concerning design and fashion museum objects, also important is a discussion about authenticity as a motor for conservation decisions. From reflections on decision-making for conservation of mass-produced objects, this thesis addresses the question, 'How to keep what was intended to be temporarily functional?'. A further contribution is a comprehensive biography of PUR fashion and design during the pioneering era.

Keywords: polyurethane; ageing processes; H-bonds; condition assessment; long-term storage conditions.

Resumo

O poliuretano (PUR) é um dos polímeros sintéticos mais difíceis de preservar. O principal objetivo deste estudo é contribuir para a avaliação do seu estado de preservação em objetos históricos e definir condições em reserva para este material perecível (20–50 anos). Com base no conhecimento atual, o PUR continua a degradar mesmo quando exposto a condições controladas (18–21°C, ≈50% HR, sem luz) e após a sua degradação, os danos são irreversíveis. As formas de degradação do PUR incluem a ocorrência de amarelecimento, desagregação, fissuração e/ou fluorescências, entre outras.

Vinte e quatro objectos de design e moda (1960s–1970s) do *MUDE – Museu do Design e da Moda, Coleção Francisco Capelo* (Lisboa) foram selecionados e estudados por microscopia ótica (radiação visível e ultravioleta), microespectroscopias de infravermelho e Raman. Para este estudo, casos de estudo nacionais e internacionais foram incluídos: espumas (à base de éter e éster), filmes (à base de éster) e fibras (à base de éter); em razoável, mau e péssimo estado de preservação. Foram ainda estudadas referências não envelhecidas (bom estado) e pré-envelhecidas naturalmente, sujeitas a ensaios de envelhecimento natural (exterior) e artificial (λ>300 nm). Com base neste procedimento, diferentes estágios de degradação do PUR são analisados, e o percurso visual (micro) e molecular do envelhecimento natural do PUR é sugerido. Os sinais de degradação do PUR são traduzidos em impressões digitais específicas do infravermelho (atribuídas a distensões N–H, C–H e C=O) e a banda a c. 1640 cm^{-1} (distensão $C=O_{urea}$) é proposta como um marcador de IV para a avaliação do estado de preservação do PUR. A suscetibilidade das pontes de H (reticulação física no PUR) a condições naturais de envelhecimento é confirmada. Para o planeamento de uma estratégia de preservação para o PUR, um ensaio de envelhecimento natural (12 meses sem luz, 45–55% HR) foi realizado para quatro condições em reserva: ambiente aberto a T ambiente; bolsas seladas a T ambiente, com/sem oxigénio e a baixa T (11–13°C). As amostras foram analisadas por colorimetria, gravimetria, ângulo de contato, dureza, microscopia ótica e microespectroscopias de infravermelho e Raman. O tratamento estatístico dos dados (ANOVA) permitiu identificar variações significativas e encontrar correlações entre linhas espectrais moleculares e aspetos físicos. O Raman provou ser fundamental na deteção de estágios iniciais da deterioração molecular do PUR e sensível a alterações moleculares responsáveis pelo aumento do amarelecimento. O acondicionamento em ambiente aberto provou ser o mais prejudicial, enquanto o acondicionamento em anoxia mostrou os melhores resultados. No que diz respeito à conservação de objetos de design e moda em museus, a autenticidade é discutida como um motor para estas decisões. A partir de reflexões sobre a tomada de decisão para a conservação de objetos produzidos em massa, esta tese aborda a questão "Como manter o que pretendeu ser temporariamente funcional?". Uma contribuição adicional é a produção de uma biografia mais completa para o PUR em moda e design durante a era pioneira.

Palavras chave: poliuretano; processos de envelhecimento; pontes de H; avaliação do estado de preservação; condições em reserva a longo-prazo.

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Symbols and Notations

Å	Angstrom
δ	Bending vibration
Δ	Variation
*ΔE**	Total colour variation
λ	Wavelength
µ	Micro
ν	Stretching vibration
A	Absorbance
AFM	Atomic Force Microscopy
Al	Aluminium
as	antisymmetric vibration
ATR	Attenuated Total Reflectance
BD	1,4-Butanediol
CAM	Comissão para Aquisição de Mobiliário
CLD	Compression Load Deflection
cm	centimetre
CPL	Cross-polarised light
DEOA	Diethanolamine
DMC	Daciano Monteiro da Costa
DMS	Dynamic Mechanical Spectroscopy
DSC	Differential Scanning Calorimetry
EO	Ethylene oxide
FOC	Fábrica Osório Castro
FTIR	Fourier Transform Infrared Spectroscopy
g	gram
GNICTMP	Grémio Nacional dos Industriais de Composição e Transformação de Matérias Plásticas
H-bonds	Hydrogen-bonding interactions
HS	Hard Segment
HS-SPME-GC/MS	Headspace-Solid Phase Microextraction coupled with Gas Chromatography and Mass Spectrometry
I	Intensity
ICI	Imperial Chemical Industries
IHRU	Instituto da Habitação e da Reabilitação Urbana
INPI	Instituto Nacional de Propriedade Industrial
IR	Infrared
kg	kilogram
kPa	kilopascal
LDPE	Low Density Polyethylene
m	metre
mm	millimetre
MMM	Maison Martin Margiela
MbOCA	4,4'-Methylene-bis(2-Chloroaniline)
MDI	4,4'-Diphenylmmethane Diisocyanate
MJ	Megajoule
ML	Metalúrgica da Longra
MoMA	Museum of Modern Art

MUDE	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo
Mw	Weight average molecular weight
nm	nanometre
OM	Optical Microscopy
PET	Polyethylene Terephthalate
PMMA	Poly(Methyl Metacrylate)
PO	Propylene Oxide
PPG	Poly(Oxypropylene) Glycols
PPL	Plane-polarised light
PTMG	Poly(oxytetramethylene) glycols
PVC	Poly(Vinyl Chloride)
PUR	Polyurethane
Py-GC/MS	Pyrolysis-Gas Chromatography/Mass Spectrometry
RH	Relative Humidity
$_s$	Symmetric vibration
s	strong
SAXS	Small Angle X-ray Scattering
SEM	Scanning Electron Microscopy
SIPA	Sistema de Informação para o Património Arquitetónico
sld	shoulder
SS	Soft Segment
T	Temperature
TDI	Toluene Diisocyanate
TEM	Transmission Electron Microscopy
T_g	Glass transition temperature
TG	Thermogravimetry
T_m	Melting temperature
TPU	Thermoplastic Urethane elastomers
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
Vis	Visible
vs	very strong
vw	very weak
w	weak
W	Watt
W	Band broadening
WAXS	Wide Angle X-ray Scattering

General Introduction

I just want to say one word to you. Just one word... Plastics...
There's a great future in plastics

The Graduate, directed by Mike Nichols (1967)

The challenge of conserving plastics

Plastics are ubiquitous and considered 'the materials of today' (van Oosten, 2009: vii). Nowadays, there is practically no field where they cannot be applied. The 20th century can be described as the 'Age of Plastic' or the so-called, 'Poly Era' (Lushington, 1967: 19). Polyamide, polyethylene, poly(methyl metacrylate), polystyrene, poly(vinyl chloride) and polyurethane are only some examples of 'poly' materials that we can easily find in our daily life objects. The triumph of plastics in the last century has been unquestionable, especially since the 1960s, where plastics chiefly became popular in art, fashion and design. Accordingly, artists such as Marcel Biefer and Beat Zgraggen state that 'plastic artefacts will be the most important witnesses to our time' (Biefer and Zgraggen, 1991 as cited in Shashoua, 2009b: 3), as they 'have shaped our culture, values, and abilities' (Madden & Learner, 2014: 5). Within the wide range of synthetic polymers, polyurethane (PUR) has definitely left its mark as a revolutionary material in the world of art and design, paving its own path in the material culture of the second half of the 20th century. There is no doubt that PUR combined freedom of creation and functionality and enabled artists and designers to conduct experiments with the material, giving shape to unusual designs and unexpected artworks that are part of museum collections. According to Colin Williamson, as plastics 'have been used by artists and designers for over 100 years', 'it is well-nigh impossible to enter a museum of modern art without seeing sculptures made from plastic' (Williamson, 2012: 15). As examples, plastics can be found in jewellery, clothing, cutlery, furniture, transportation, toys, photography, art and certainly, in almost every major museum in the world (Williamson & Quye, 1999). MUDE, the design and fashion museum in Lisbon, is an example of such place and the holder of the PUR case studies of this research.

From a different point of view, conservators may describe the task of preserving a plastic object as an ungrateful mission, launching provocative questions such as 'Are plastics worth preserving?' (Mossman, 1993: 30), or even questions with no friendly answers, such as, 'How long will our plastics collections survive?' (Mossman, 1993: 25). As some authors have been discussing, it is already acknowledged that conserving plastics poses demanding challenges (Shashoua, 2009b; Lavédrine *et al.*, 2012a). Thousands of different polymers can be used to produce a plastic, and beyond this fact, plasticisers, stabilisers, colorants, fillers and processing aids (among others) can be added to a plastic

formulation (Williams, 1993). As a result, depending on the plastic composition, the exposure to oxygen, light or moisture (among other factors) can promote polymer degradation reactions. A wide range of ageing behaviours and degradation forms can be found in plastic items, and in general, the lifespan of plastics is short (compared with those of 'traditional' materials) (Shashoua, 2009b). It is well known that plastics deteriorate continuously and 'prolonging the useful lifetime of plastics by inhibitive conservation is possible today but is very limited in scope and effectiveness' (Shashoua, 2009b: 16). Plastics are easily degraded by light, heat, oxygen and water, and 'once initiated, degradation of plastics cannot be prevented, reversed or stopped' (Shashoua, 2009b: 16). In some cases, degradation can start within 5–50 years, and thorough research into this field has only recently started (c. 25 years ago). From the survey of museum collections holding plastic objects (e.g. Victoria and Albert Museum), cellulose nitrate and acetates, poly(vinyl chloride), polyurethanes and rubbers have been identified as the most prone to deterioration (Keneghan, 2002). Among these plastics, PUR is considered the most difficult synthetic polymer to preserve (Garside and Lovett, 2006), showing (in general) a lifespan of c. 30–50 years. In sum, inconvenient truths about plastics conservation cannot be ignored and new ways should be explored to prolong the lifespan of plastic objects. Susan Mossman suggests the production of thorough records as a first conservation approach to preserve a plastic artefact (Mossman, 1993) and John Morgan, the thorough development of preventive measures (Morgan, 1993). As identified by the author, 'It is already clear from the work to date that if plastics are to survive they will require more in the way of preventive conservation than has hitherto been given to most other materials' (Morgan, 1993: 43). Either way, great advances have been achieved and research focused on the understanding of plastics degradation has grown significantly in the last years.

Polyurethane in the MUDE collection – the motivation behind the study

The MUDE collection, displayed in downtown Lisbon since 2009, holds c. 2000[1] design and fashion objects mainly from the 20th century. Due to the renowned authors represented and the historical significance of the heritage asset gathered by the private collector Francisco Capelo, this collection was acquired by the Lisbon City Council in 2002 (Coutinho, 2014). Up to 2009, part of this collection was displayed in Centro Cultural de Belém (Lisbon) and only in 2009, MUDE's doors opened to the main public. For the opening, important pieces from this heritage of excellence were displayed, and among them, design icons made of PUR.

PUR was one of the most popular industrial novelties during the 1960s and 1970s, changing the world of fashion and product design during this period. Within the MUDE collection (as in other museums),

[1] This number includes the asset gathered by Francisco Capelo and the most recent acquisitions of MUDE: Eduardo Afonso Dias, Daciano da Costa and António Garcia collections.

many objects are living proof of this fondness for PUR. From furniture design to ready-to-wear fashion garments and accessories, the MUDE collection shows how PUR has come into every home in the form of comfortable, unusual and stylish objects. Polyurethane foams, rubbers, artificial leathers, films and fibres were used by designers, and can easily be found in objects from the MUDE collection (Figs. 1 and 2).

Figure 1 Examples of objects from the MUDE collection made of PUR coatings. Joe Colombo, *Tube* chair, 1969-70 (left) and Achille Castiglioni, *Primate* kneeling bench, 1970 (right). Photos: © MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

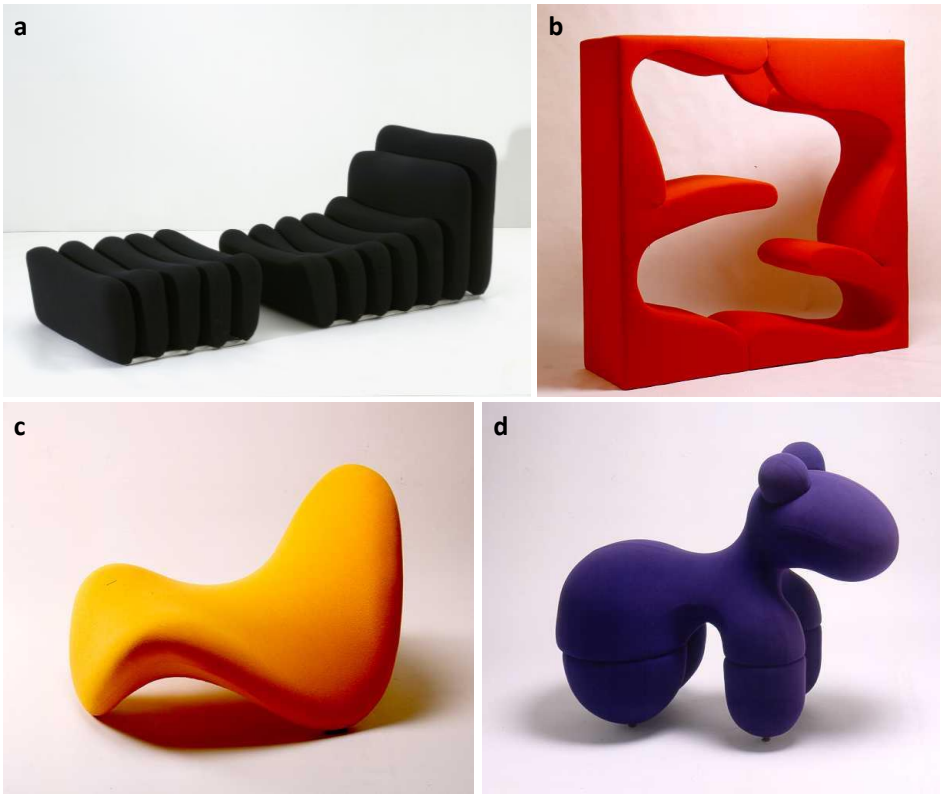


Figure 2 Examples of objects from the MUDE collection made of PUR foams. Joe Colombo, *Additional Living System* lounge chair, 1967 (a) Verner Panton, *Living Tower* (or *Pantower*) seating system, 1968–1969 (b); Pierre Paulin, *Tongue Model No.577* seat, 1967 (c); and Eero Aarnio, *Pony* seat, 1973 (d). Photos: © MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

As shown in Figs. 1 and 2, the large material diversity of the MUDE collection is evident and the conservation problems raised by this heritage are most similar to those found in contemporary art museums. Polyurethane, as one of the most difficult synthetic polymers to preserve, was identified in this collection as a conservation priority. Several PUR-based case studies show a high level of instability, clearly evident by crumbling (Fig. 3), brittleness, bloom, chalking (Fig. 4), tackiness and yellowing, depending on the type and form of polyurethane.

Figure 3 Archizoom Associati, *Safari* sofa, 1968. Top: General view. Bottom: Detail of the collapsed foam padding in 2012 (showing an intense brown colour).

Figure 4 Achille Castiglioni, *Primate* kneeling bench, 1970. Condition of the ester-based PUR artificial leather in 2012, with white powder at the surface (chalking) and formation of cracks. Top: overall image of the upper part of the seat. Bottom: detail of the white powder and cracks.

At least 20% of the MUDE collection[2] may include PUR elements, as this polymer could be the material with the highest deterioration rate.

Conservation studies regarding PUR have been focused mainly on PUR foams. Consequently, the knowledge about the PUR wide range of materials is still insufficient and the conservator is not sure about what to expect in the future from objects made of these materials. Studies focusing on storage conditions for PUR polymers are lacking, as well as on cleaning, consolidation and stabilisation methodologies for polyurethane rubbers, coatings, adhesives and fibres. Above and beyond, it may be concluded that after degradation starts, PUR continues to degrade even if exposed to controlled conditions (such as 18–21°C and 50–55% RH, in the dark). PUR degradation at the moment is inevitable and could take place within a few decades. In addition, the high risk of loss caused by the PUR fast deterioration rate is not exclusively related to the loss of materials. As known, losing historical and iconic objects from the history of the 20th century implies the loss of important testimonies from design, fashion, industrial, chemical, social, political and economical contexts, and with that, the loss of testimonies from our material culture.

By taking these statements into consideration, a large percentage of the MUDE collection may be at risk, and difficult decisions about the preservation of these objects will have to be made in a near future. It is vital to expand the knowledge about PUR history and use by designers, and to define preservation conditions and conservation priorities. Finally, it is also crucial to discuss preservation options for these historical objects. Acknowledging that PUR has a short lifespan, and that conservation aims 'at safeguarding tangible cultural heritage, while ensuring its accessibility to present and future generations' (ICOM-CC, 2008: n.p.), 'What does the future hold for PUR fashion and design?' is the main question to which this thesis intends to react by focusing its research into the establishment of practical solutions for PUR conservators. However, this thesis does not intend to give a final answer to the question (shown as the thesis title), but to draw attention to the challenges of PUR conservation. In sum, this thesis attempts to propose conservation solutions for one of the most problematic plastics in museum collections, PUR.

Scope and outline of the thesis

The primary purpose of the present research is to contribute to the knowledge of polyurethane conservation, already identified as one of the most difficult synthetic polymers to preserve. To achieve this goal, this thesis analyses in particular the conservation issues raised by the presence of this material in product design and fashion objects, dated from the 1960s and 1970s. Focused on twenty-

[2] This estimation is based on information on labels, visual (macro) assessment and bibliographic research.

four selected national and international PUR-based historical objects from the MUDE collection, this research attempts to explore the historical, the molecular and the preservation frameworks of PUR. It aims at contributing to a comprehensive biography of PUR during this period, to a new insight into PUR degradation, and to the development of preservation strategies for this highly ephemeral material. In this thesis, PUR foams (ether- and ester-based), coatings (ester-based) and fibres (ether-based) have been included, and within foams, slabstock, moulded and quasi collapse foam processes were selected. This highlights the multiplicity of PUR forms focused in this thesis, contradicting the research tendency of conservation studies, mostly focused on PUR foams.

Since the history of product design and fashion garments during the time frame of the present research has been focused on the literature, this subject is beyond the scope of this study. Conversely, little attention has been given to a more complete history of PUR, including the documentation of its entrance and relevance in the world of fashion and design and the relationships of the material with entrepreneurs and designers. To this end, this thesis has focused on the work of Bayer, Gufram and Poltronova Italian design companies, and on the Portuguese context of PUR industries and design, by examining selected case studies from MUDE as testimonies of a historical framework.

Concerning the study of ageing pathways of PUR, as the carrying out of artificial ageing experiments has been the most common approach in conservation research, this thesis attempts to focus its attention on the characterisation of natural ageing processes. From this, it aims at accurately tracing degradation in naturally aged artefacts and to translate condition grades into specific visual (at the micro level) signs and spectral lines. However, it is not the purpose of this study to introduce novel analytical techniques to assess ageing processes, but rather to explore in-depth the potential of common evaluation methods used in conservation – optical microscopy, and infrared and Raman spectroscopies. The data obtained can be compared with a broader body of published information. From this investigation, the particular success of each technique in the detection and characterisation of ageing is stressed by highlighting their advantages and weak points. Moreover, the present thesis has disclosed a new insight into polyurethane degradation. To this date the study of hydrogen-bonding interactions (H-bonds) in PUR foams has been mostly restricted to polymerisation, with a few studies suggesting the susceptibility of these secondary bonds to both high humidity and high temperature. With the present investigation, H-bonds have been demonstrated as being highly unstable and affected by exposure to natural ageing conditions by means of infrared and Raman spectroscopies. Based on optical microscopy, the fluorescence of PUR under blue-violet and ultraviolet excitation wavelengths is also explored and studied in detail. For the first time, the molecular groups responsible for PUR fluorescence are suggested and PUR fluorescence with ageing is followed under the microscope.

Regarding practical solutions for conservation, given that storage conditions have not been defined for PUR, this study offers for the first time a proposal of a guideline for the long-term storage of PUR polymers based on the thorough assessment of an ageing experiment in the dark. However, the guideline designed in this thesis is strictly limited to the results of a one-year experiment in the dark. Still, the ageing is ongoing and the final set of uncollected samples can be assessed in the future.
Concerning design and fashion objects in museum collections, a discussion about authenticity as a motor for conservation decisions is also an important topic in the present study, highlighting some particularities of conserving and communicating design, as opposed to works of art.
The time-frame of the 1960s and 1970s has been selected because of its chronological relevance in the use of PUR in art, fashion and design, and also because MUDE holds several PUR-based objects from this period, showing degradation. Consequently, the focus of this research on this specific period may allow the sharing of promising results with museums holding similar collections and having comparable conservation issues.

This thesis is divided into the following chapters:

Chapter 1 – State of the Art, presents a brief historical review of PUR knowledge from molecular and conservation perspectives. It reviews what has been mentioned about PUR advent and its chemistry, and summarises the main conclusions about PUR deterioration and conservation (active and preventive). Also, it focuses on the entrance of plastics in the fields of fashion and design. This chapter aims at providing the background knowledge for the three main subjects of the present thesis: PUR biography, natural ageing assessment and preventive measures for PUR storage.

Chapter 2 – Contributions to a Biography of Polyurethane — From the Industry to the Daily Life of the Consumer, contributes to a comprehensive history of PUR by studying the introduction and relevance of the material in areas such as product design and fashion during the 1960s and 1970s. It documents the relationships established between PUR entrepreneurs and designers, and the key reasons that led designers to select this material over others. To achieve this goal, this chapter gives an insight into the industrial patents filed during this period and to the particular work of firms such as Bayer (inventor of PUR in 1937), Gufram and Poltronova (important design companies from the Italian landscape) with PUR. Moreover, this chapter documents the foundation of PUR industries in Portugal and the work of Portuguese designers with this material.

Chapter 3 – Degradation Studies for PUR-based Case Studies from the MUDE Collection, is focused on the assessment of PUR ageing in historical objects from this collection. To this end, PUR-based

objects showing foams (ether- and ester-based), coatings (ester-based) and fibres (ether-based) made of PUR are selected, as well as objects showing different condition grades (from fair to unacceptable). From this selection, the objects condition is discussed by a thorough infrared spectroscopy and optical microscopy analysis of the PUR, with a special focus into the changes of hydrogen-bonding interactions upon ageing. As the singular analysis of the case studies suggest characteristic infrared and visual pathways of PUR natural ageing, this chapter also discusses ageing experiments (artificial and natural) on model samples and the correlation of the obtained results with the case studies.

Chapter 4 – Conservation Studies for Polyurethane, is focused on the study and discussion of conservation practices for PUR. The establishment of preventive measures for the long-term storage of PUR is studied throughout the assessment of natural ageing experiments in the dark for foams (ether- and ester-based) and coatings (ester-based). The results obtained from the ageing assessment highlight the efficacy of Raman spectroscopy in the evaluation of PUR early stages of deterioration. In addition, this chapter discusses, from a theoretical point of view, the curatorial and conservation practices adopted in museums for PUR-based objects showing degradation or considered total losses. To this end, a brief review of the literature is presented, as well as its complementation with the results obtained from an online survey into the experience of conservators and curators with PUR ephemeral nature.

Chapter 5 – Concluding Remarks and Future Perspectives, closes this thesis by presenting the most important conclusions and future work on the field of PUR conservation research.

CHAPTER 1

STATE OF THE ART

1.1. Polyurethane advent and chemistry

1.1.1 A brief history of Polyurethane

There is probably something made of the material our team developed in every home and every car in the world: mattresses, refrigerators, bumpers, steering wheels, dashboards, shoes (…) It is a pleasant feeling to be able to look back on it all at the end of my life.

Günter Oertel for Bayer's Anniversary Book, 2013 (Oertel, 2013: 65)

The history of polyurethane (PUR) chemical development has been widely studied by former and current workers of polyurethane industry and researchers of polymer chemistry. Among them, Günter Oertel (1932–2013) is definitely one of the main figures. According to Joachim Wolff[3], he "is considered one of the pioneers of polyurethane chemistry' and 'His research resulted in more than 90 international patents and countless publications' (Wolff as cited in Dr. Günter Oertel Passes, 2013). Still, during this investigation, one of the first conclusions was that although the history of PUR has been widely studied, few pages have been commonly dedicated to this subject. In order to provide a deeper insight into the history of PUR, this section reviews the information already published, especially concerning the chemical history of the polymer up to the 1970s and taking into account both primary and secondary sources[4]. Here the reader can find an introduction to the history of polyurethane which summarises its inventors, companies, discovery dates, material achievements and most common commercial trade names up to the 1970s. All these aspects are described concerning the wide class of polyurethanes: foams, coatings, fibres and rubbers, among other forms. Since few references concerning the novelty of polyurethane and its acceptance by the public were found, this section is also the starting point for deeper research work presented in Chapter 2 (p. 49).

The history of polyurethane chemistry began with Otto Bayer and his collaborators in I.G. Farbenindustrie A.G. a subdivision of Bayer Corporation, at Leverkusen, Germany, in 1937 (Prisacariu, 2011; Hepburn, 1992; Ashida, 1995b; Verg, 1988; Hirtz & Uhlig, 1985). At this time, the company was attempting to discover a novel and rival material, capable of competing with nylon 6,6 patented by Wallace H. Carothers and co-workers of E.I. DuPont de Nemours & Co., Delaware, in USA, in the 1930s (Hepburn, 1992; Ashida, 2007; Verg, 1988; Morgan, 1981). According to K. Ashida, the introduction of nylon 6,6 'was a big stimulus to chemists for pioneering synthetic polymers' (Ashida, 2007: 5).

[3] Head of the Polyurethanes Business Unit and member of the Executive Committee of Bayer Material Science.

[4] As examples of those sources, industrial patents, scientific books (thematic, handbooks and a polymer science dictionary), publications concerning the Bayer Company's biography and research articles were accessed. The whole set of patents was available from the online databases Espacenet, Patent search of the European Office and Google Patent Search platform.

Polyurethanes, which came into being shortly after, could be considered one of the most successful outcomes of this motivation.

Although the tribute of polyurethane invention is given to Otto Bayer (head of Bayer's Main Scientific Laboratory from 1934 to 1951), the development of aliphatic and aromatic diisocyanates is credited to Wurtz and Hoffmann before 1850 (Prisacariu, 2011; Hepburn, 1992). To O. Bayer is attributed the use of isocyanates in polymer formation as well as the development of the diisocyanate polyaddition process (Hepburn, 1992; Prisacariu, 2011). According to his testimony, 'What I had in mind was a process which would enable the construction of macromolecules by letting two low-molecular compounds react with one another in a polyaddition phase, without either co reactant splitting off.' (Bayer, n.d., as cited in Verg, 1988: 287). In the 1930s, this idea resulted in the production of polyurethane, firstly registered in the German Patent 728,981 (Szycher, 2013). This patent introduced the use of aromatic and aliphatic diisocyanates and ether- and ester-based diols to produce fibre-forming polyurethane (Prisacariu, 2011; Szycher, 2013). Nevertheless, Otto Bayer's superiors paid little attention to this discovery (Szycher, 2013; Schneider, 2013). At the beginning of his experiments, Bayer's intention to produce a fully synthetic fibre based on a polyaddition reaction was called a 'crazy idea' and for his supervisor, maybe he was not 'the right man to manage this laboratory after all' (Schneider, 2013: 54). Nonetheless, Bayer did not give up of his idea and in 1937 the first polyurethane patent was filed.

Besides the I.G. Farbenindustrie, 'independent studies were also being carried out in Japan at the Tokyo Institute of Technology as well as at the E.I. DuPont de Nemours & Co.' (Ashida, 2007: 5). DuPont, also one of the leading companies of polyurethane chemistry, patented reactions between diisocyanates and hydrogen-containing compounds in 1942 (Szycher, 1988). Therefore, the main achievements of the polyurethane industry during the 1940s–1970s were divided between Bayer and DuPont.

Regarding the beginning of polyurethane wide polymer class, although until 1940 only linear PURs were being focused upon, wider applications were shortly achieved (Hepburn, 1992). The promising reaction between isocyanates and OH groups led to the production of a tailor-made polymer class that included linear, branched and crosslinked polyurethanes (Prisacariu, 2011). From these reactions, fibres, films, rubbers, solids and foams started to be produced (Prisacariu, 2011). As examples, thermoplastic urethane elastomers (TPUs) were firstly commercialized in 1942, in Germany, under the trade names *Igamid U*[5] and *Perlon U*[6] (Szycher, 1988: 298; Szycher, 2013: 1). These materials were

[5] *Igamid U* was produced based on the reaction of 1,6-hexamethylene diisocyanate (HDI) with 1,4-butanediol. Its properties are similar to nylon 6,6, but its T_m is about 183°C. Later similar materials were designated *Durethan U* (Alger, 1996: 256).

[6] *Perlon U* was produced based on the reaction of 1,6-hexamethylene diisocyanate (HDI) with 1,4-butanediol, i.e. the 6,4-polyurethane. Its T_m value is about 183°C and it has similar properties to nylon 6,6, although textiles based on the polymer are rather harsh and stiff (Alger, 1996: 365).

invented by Farbenfabriken Bayer (Germany) with the aim to replace the natural rubber used during World War (Prisacariu, 2011). At first these rubbers were known as *I-rubbers*[7] and showed poor properties but soon they became famous by their higher abrasion resistance, strength, good flexibility, elasticity, and resistance to oxygen (Meckel *et al*., 1996: 16; Prisacariu, 2011: 1). The product *Perlon U* was the first polyurethane rubber used to produce a TPU fibre with the aim to replace nylon; however, it showed inferior properties (Cook, 1984). For this reason, this fibre was not successful during World War II serving mostly the production of brush bristles and filtration fabrics (Cook, 1984). One highly known TPU rubber from the fifties was *Vulkollan*® from Bayer (Bayer *et al*., 1950 as cited in Hill *et al.,* 1956: 927). Nevertheless, the Imperial Chemical Industries, Ltd., ICI (London, UK) and DuPont were also commercializing these products under the trade names *Vulcaprene*® (Harper *et al*., 1948: 61 as cited in Hill *et al.,* 1956: 927) and *Adiprene*® (Hill *et al.,* 1956: 927), respectively. Concerning the production of polyurethane foams, the first patent involving this material and simultaneous reactions (polyurethane formation and gas generation) was registered in 1942 by K. Zaunbrecher and H. Barth of Farbenfabriken Bayer Aktiengesellschaft (Arnold, *et al*., 1959: 47 as cited in Ashida, 1995a: 13). In this method, a reaction between a diisocyanate and a polyester-based polyol in the presence of water is described, along with the formation of carbon dioxide and polyurea (Ashida, 1995a). However, the first experimental attempts came from the testing unit in 1941 with the description 'suitable at best for the manufacture of imitation Emmentaler cheese' (Polyurethanes – a new class of plastics, as cited in Verg, 1988: 288) and it took more than ten years for polyurethane foams to enter the industrial market. According to Szycher, these foams were called *Troporit M*® and 'were used to produce aircraft propeller blades, and rigid, foam filled landing flaps and skis' (Szycher, 1988: 298). In the following years, further developments were achieved, for example, the commercial availability of polyisocyanates since 1952 (such as diphenylmethane diisocyanate, MDI and toluene diisocyanate, TDI) and polyether-based polyols since 1957, by the E. I. DuPont de Nemours and Co. and the Dow Chemical Co. (Michigan, USA) (Hirtz & Uhlig, 1985; Sonnenschein, 2015). Since then, the production of polyurethane flexible foams has grown rapidly, in particular, due to the lower costs and improved hydrolytic stability of polyether-based polyols (Hirtz & Uhlig, 1985). Polyester-based polyols were gradually replaced and soon polyether polyols became one of the major compounds in the polyurethane foam industry (Ashida, 2007). As cited by Hirtz and Uhlig, 'in 1960, already more than 45 000 tons of flexible polyurethane foams were produced' (Hirtz & Uhlig, 1985: 1). The use of chlorofluoroalkanes as blowing agents, polyether-based polyols and MDI opened the world of polyurethane production to rigid foams in the 1950s (Hirtz & Uhlig, 1985). These foams were especially

[7] Trade name for an early polyurethane elastomer made by reaction of hydroxyl-terminated polyester prepolymer and diisocyanates with a small amount of trimethylolpropane to give limited crosslinking (Alger, 1996: 256).

used as thermal insulation materials but with the development of novel semi-rigid and integral foams, components for the interior of automobiles and shoe soles were also being produced. In 1968, *Bayflex*™ was a well-known polyurethane foam product from Bayer to produce shoe soles (Schneider, 2013).

With the development of injection moulding and extrusion processes, in 1969, the RIM (Reaction Injection Molding systems) technology has born and the world of polyurethane possibilities was greatly extended (Hirtz & Uhlig, 1985; Sharmin & Zafar, 2012). From this moment, it was possible to produce PUR plastic parts based on the combination of two liquid components that chemically reacted in a closed mould, without the requisite of high temperatures and pressures. One example of an iconic design object made of polyurethane rigid foam is the *Panton* chair designed by Verner Panton in the mid-1950s[8] (at that time, called the *S*-chair) and produced in 1968–1971 with Baydur™ (trademark from Bayer since 1960) (Schneider, 2013; Remmele, 2000). Although this chair was first constructed in plywood by the furniture manufacturer Thonet (Vienna), Verner's original idea was to use plastic. Nevertheless, only in 1968 was his wish entirely granted with the use of PUR rigid foam (Fig. 1.1) (Remmele, 2000). Early attempts were carried out using fibreglass-reinforced polyester resin; however, due to the high thickness of the material, the goal of producing a stackable chair was compromised. With the introduction of *Baydur™*, this drawback was overcome and the *Panton* chair was produced in seven different colours through a joint partnership between Bayer and the Swiss design company Vitra (Remmele, 2000). Nowadays, the chair is still produced with high resilient polyurethane foam as well as other materials such as polypropylene.

Regarding the application fields of polyurethane, while flexible and rigid foams were mostly used for furniture design, insulation purposes and automobile industries, polyurethane coatings were mostly used in the textile industry with the production of synthetic leathers and breathable fabrics. As examples, B.F. Goodrich (Ohio, USA) developed *Estane*® in the early 1960s and Bayer *Desmopan*®[9], in 1962 (Meckel *et al*., 1996: 16; Prisacariu, 2011: 2; Verg, 1988: 394).

> *What links waterproof, breathable films for rain jackets with sheathing for power cables on oil platforms? (...) In 1962, Bayer introduced a line of rubber-like elastomers that bridged the gap between rubber and rigid plastics. They were thermoplastic polyurethanes (TPU). The product name: Desmopan™. Their appearance: transparent to white granules. Their most outstanding characteristic: the rigidity and flexibility of the different grades can be varied widely, making them stable over a broad range of temperatures. They are design-friendly and chemically resistant. They are resistant to scratches, tears, cuts and abrasion, but still flexible* (Schneider, 2013: 56–57).

[8] Other examples of design objects based on PUR polymers are shown in section 1.4, p. 37.

[9] *Desmopan*®: partially crosslinked thermoplastic polyurethane elastomer based on polyester or polyether polyol and MDI (Alger, 1996: 127).

Figure 1.1 Verner Panton, *Panton* chair, 1968, coated and varnished polyurethane structural foam from the MUDE collection. Photo: © MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

Also in the textile industry, polyurethane elastic fibres were developed. In the fifties, this goal was achieved by DuPont with the invention of *Lycra*®, which enabled the production of stretch-to-fit apparel and the replacement of cotton-wrapped rubber elastics (Morgan, 1981; Blaszczyk, 2006; Moncrief, 1975: 489 as cited in Legge, 1989: 530). This invention could be found in the patent 'Elastomers from polyalkylene ether glycol reacted with arylene diisocyanate and water' (Langerak *et al*., 1954). At first this fibre was called *Fiber K*, but since 1958 the trade name *Lycra*® was adopted and the commercial production started in 1960–1961 (Carraher, 2013: 287; Cook, 1984; Morgan, 1981). The textile industry has found in polyurethanes the solution to produce spandex fibres since they can be tailored into desirable properties. According to J. Gordon Cook, 'the lack of flexibility of the pliable constituent (with low melting point) was overcome by using preformed segments of molecule of

considerable size (the 'soft' segments)'; and 'the cohesion of the interchain bonding constituents ('hard segments') was assured through the use of urethane or urea groups' (Cook, 1984: 614). This resulted in the production of polyurethane spandex fibres which were stronger than rubber and with greater recovery power. These fibres are prepared by a spinning process with polar solvents and consist of at least 85% segmented polyurethane (Carraher, 2013). Based on the combination of these elastic fibres with cotton, polyamide, polyester and acrylic fibres, the production of lightweight, elastic and washable fabrics has been achieved (Morgan, 1981). Lingerie, sportswear and swimwear are examples of clothes which have benefited from this invention, especially due to advantages such as low maintenance, mass-market apparel and comfort (Morgan, 1981; Blaszczyk, 2006). As cited by Blaszczyk, 'Lycra's worldwide earnings skyrocketed to $6.3 million in 1964 and topped $30 million in 1969', and 'by 1971, Lycra was among DuPont's most profitable products, yielding a 30 percent return on investment', which proves the dramatic success of this fibre during this period (Blaszczyk, 2006: 519).

During the 1970s, the polyurethane market showed one of the highest growths and large chemical companies started to dominate the polyurethane industry, in particular, Bayer, BASF (Germany), ICI and Dow Chemical (Prisacariu, 2011). The use of toluene diisocyanate (TDI) was dominant in the production of slabstock polyurethane foams and 4,4'-diphenylmmethane diisocyanate (MDI) found a wider application in fibres and elastomers. If once polyurethane was mostly used as an interior material (unseen), in the sixties and seventies it expanded to visible applications which included 'automobile bumpers and fascia, armrests, body panels, shoe soles, furniture, window frames, sports equipment, electronic cabinets, athletic surfaces, and bicycle seats' (Hirtz & Uhlig, 1985: 2).

In the 1980s, the polyurethane business developed on a global basis, especially, between Europe and USA. Although Bayer continued to be the technological leader of the industry, other companies have emerged as manufacturers of polyurethane. For example, BASF became a strong manufacturer of polyurethane raw materials, ICI developed the production of MDI during this decade and Dow started to focus on the manufacture of polyether-based polyols and TDI (Prisacariu, 2011). During the 1990s, China started to appear as a strong producer of polyurethane products, spreading this business to continents other than Europe and America (Prisacariu, 2011). Besides the globalisation of the industry, environmental issues resulted in changes on the polyurethane formulations. As examples, the rising awareness towards the hazards of using chlorofluoroalkanes as blowing agents resulted in their replacement by carbon dioxide, pentane, 1,1,1,2-tetrafluoroethane and 1,1,1,3,3-pentafluoropropane; and, an interest in the use of vegetable oil based polyols (renewable bio-based components as raw materials) could be named (Sharmin & Zafar, 2012).

In the 20th century, the continuous development of the Chinese economy has resulted in a significant growth of polyurethane production. For instance, according to PUR expert Robin Grieve (2003), 50%

of the shoe sole industry was being done in China in the early 2000s. Furthermore, during the next 10 years, 50% of the polyurethane-manufactured goods 'will be in China with the other 50% shared between the United States and Europe' (Grieve, 2003: 117).

As stated in Bayer's anniversary book (2013), polyurethanes 'are diverse, versatile and almost infinitely variable', they can be 'rigid or brittle, soft or elastic, dull or tacky', and 'they can also be foams' (Schneider, 2013: 54). In simple words, polyurethanes are 'the chemist's dream material' and 'the material with unlimited uses' (Schneider, 2013: 54).

1.1.2. Raw materials, polymerisation processes and morphology

The wide range of materials offered by polyurethanes is undeniable. Foams, rubbers, fibres, films, coatings and adhesives are only some examples of those possibilities. Nevertheless, this unlimited quality results from the potential to produce tailor-made polyurethane formulations. It is fundamental to understand the variety of raw materials involved, the polymerisation processes and the polymer final morphologies. Although these subjects have been highly focused on by chemical researchers, this knowledge has not been explored to the same extent by conservation scientists or conservators. Consequently, these subjects are briefly reviewed in this section in relation to polyurethane flexible foams and films, since these are the most common polyurethane forms found in the MUDE collection. For that, the base literature has mainly been focused on the research work conducted by renowned chemists such as James H. Saunders, Kurt C. Frisch, Günter Oertel, Ashish Aneja, Garth L. Wilkes, James P. Armistead, Ralph D. Priester, Robert B. Turner, Bryan D. Kaushiva, Gerd R. Rossmy and Michael Szycher. Polyurethane foams will be abbreviated to *PUR foams*, and polyurethane films (or coatings) to *TPU films*.

PUR foam is known as one of the most versatile polymers (Szycher, 2013). It belongs to the class of cellular plastics (or plastic foams), which consists on two-phase systems comprising a solid-polymer matrix and a gas-phase (Landrock, 1995). This class of polymers had a tremendous impact in the plastics industry, which according to Kaneyoshi Ashida, has resulted in 'a new era of plastics' and in the purported 'Plastic Foam Age' (Ashida, 1995a: 11). The potential to produce tailor-made formulations is one of the most attractive qualities of this polymer and it is largely related to the unlimited possibilities of polyurethane macroscopic cell structure and morphology. Moreover, it is one of the reasons why this polymer became a leading figure of this Plastic Foam Age (Ashida, 1995a: 11).

In relation to material forms, PUR foams can be flexible or rigid, depending on the crosslinking degree, which, in turn, is a consequence of their chemical composition (Landrock, 1995). Within foams, two

types of production can be named, slabstock and moulded processes. This section will start by discussing slabstock foams, following to moulded foams.

For the formation of PUR flexible foams several raw materials are employed. Polyols, isocyanates, water, catalysts and surfactants are the main components of a typical slabstock foam formulation. The formation of PUR flexible foams is relatively fast (1–3 min), highly exothermic (75–150°C total temperature rise) and involves a significant increase in volume (20–50x) until cell rupture takes place (Armistead *et al.*, 1988; Artavia & Macosko, 1994). The designation 'polyurethane' is mainly due to the urethane linkage (–NH–COO–), which is formed by the reaction of diisocyanate with hydroxyl groups (Ashida, 2007; Oertel, 1985). Depending on the polyol chemical family, these foams can be classified into ether- or ester-based, the first being the most commonly produced since the 1960s (Ashida, 1995b, 2007; Oertel, 1985; Szycher, 2013). Regarding the isocyanates, aromatic compounds have been the preference choice for PUR foams (Ashida, 2007; Oertel, 1985). In summary, the typical chemical composition of PUR slabstock flexible foams is based on ether-based polyols (e.g. polypropylene oxide glycol, Fig. 1.2) and toluene diisocyanate (TDI) (Fig. 1.3). The former is widely used as a mixture of 2,4- and 2,6-isomers, in the weight ratio of 80/20 and the polyol is usually a trifunctional polyether (triol) with c. 3000 Mw, providing the covalent crosslinking points (Armistead *et al.*, 1988; Ashida, 1995b, 2007). The preferential choice for ether-based polyols is mainly due to low production costs, high hydrolysis resistance, low viscosity, choice of functionality and equivalent weight (Ashida, 1995b).

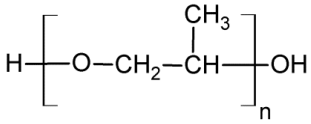


Figure 1.2 Polypropylene oxide glycol (PPO).

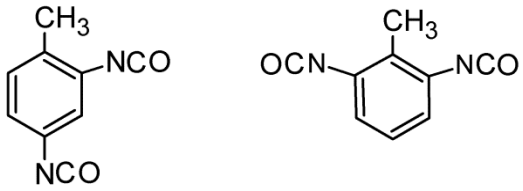


Figure 1.3 Toluene diisocyanate (TDI). Left: 2,4-TDI. Right: 2,6-TDI.

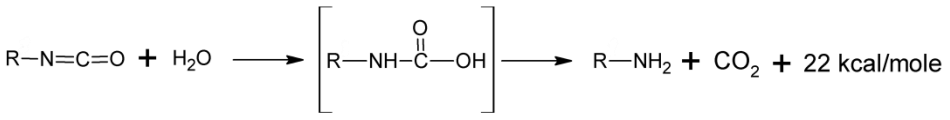
Although diisocyanates and polyols are considered the building blocks of polyurethane structure (Ashida, 2007), blowing agents (such as water), surfactants and catalysts also play an important role in the formation of PUR supramolecular structure (Bailey & Critchfield, 1981; Oertel, 1985; Szycher, 2013). The main blowing agent for PUR flexible foams is water. This compound reacts with isocyanate

groups leading to carbon dioxide and heat, which consequently, blows the initial viscoelastic liquid into a three-dimensional foam polymer (chemical blowing agent). Besides this agent, physical blowing agents can also be applied, as well as combinations of both (Ashida, 1995b; Szycher, 2013). Unlike water, these physical blowing agents, hydrocarbons and halogenated hydrocarbons, do not react with isocyanate groups and show low boiling points (below 50°C) (Szycher, 2013). In this way, they vaporize along with the exothermic foaming reaction (Ashida, 1995b; 2007). As surfactants, the industry has made use of polysiloxane–polyether block copolymers (Kaushiva *et al*., 2000). These compounds play an important role in the control of cell structure and in the stabilisation of the foam rising process (Armistead *et al.*, 1988; Ashida, 1995b). In relation to catalysts, two classes are used in PUR foams production. Tin compounds contribute to the urethane formation reaction (gelation catalysts), whereas tertiary amines accelerate both the generation of gas and the urethane formation (blowing and gelation catalysts) (Artavia & Macosko, 1994; Ashida, 1995b, 2007). Therefore, based on the combination of the whole set of raw materials, the final PUR foam product can be tailor-made into desired properties and unlimited possibilities of supramolecular structures are designed.

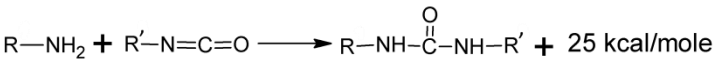
The subject of polyurethane macro- and micro-morphology, however, has been a challenging question in chemical research[10]. For these studies, different visual, mechanical and spectroscopic techniques have commonly been applied. As examples, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) have been used to study the segmented structure of polyurethanes and the urea aggregation behaviour; dynamic mechanical spectroscopy (DMS) and differential scanning calorimetry (DSC) to study the changes in the polymer modulus and soft segment glass transition temperatures; infrared spectroscopy (FTIR) to follow the kinetics of reaction sequences during foam rising; wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) to study the presence of microphase separation and to provide structural information at length scales ranging from c. 10 to 500 Å; scanning transmission X-ray microscopy (STXM) to characterise the composition of macrophase-segregated block copolymers using low energy and high spectral resolution; and last, time-domain nuclear magnetic resonance spectroscopy (TD-NMR) to identify and quantify hard and soft domains with low and high segmental mobility. From these studies, important conclusions have been drawn. It is now generally accepted that polyurethane foams are segregated structures comprising a two-phase morphology of the solid state (soft and hard segments, SS and HS) and two types of crosslink (chemical and physical) (Armistead *et al.*, 1988; Priester *et al*., 1990; Aneja & Wilkes, 2002). In addition, two primary reactions have been mentioned as involved in the production of PUR foams, (i) and (ii):

[10] See for example, Cooper & Tobolsky (1966), Merten *et al*. (1968), Armistead *et al.* (1988), Priester *et al*. (1990), Moreland *et al*. (1991), Thomas *et al*. (1994), Elwell *et al*. (1996), Kaushiva & Wilkes (2000), Kaushiva *et al*. (2000), Rightor *et al*. (2002), Lan *et al*. (2014), Aou *et al*. (2015), and Yilgör *et al*. (2015).

(i) The blowing reaction (gas formation), as shown in equations 1.1 and 1.2 (Priester & Turner, 1994: 80; Kaushiva, 1999: 5).



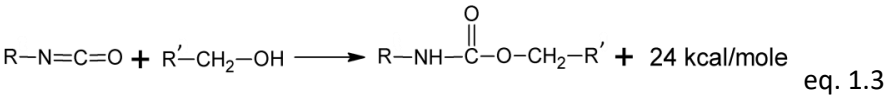
eq. 1.1



eq. 1.2

At first, the exothermic reaction between water and the diisocyanate leads to unstable carbamic acid (R–NH–COOH) which decomposes into an amine ($R–NH_2$) and carbon dioxide (CO_2). Consequently, the formed amine continuous to react with other isocyanate groups and forms the urea linkage (–NH–CO–NH–), which chain extends polyurea segments (Armistead *et al.*, 1988).

(ii) The gelation reaction (urethane linkage formation), is shown in equation 1.3 (Priester & Turner, 1994: 80; Kaushiva, 1999: 7).



eq. 1.3

The urethane linkage (–NH–COO–) results from the exothermic reaction between hydroxyl groups (of the polyol) and other isocyanate groups (Aneja & Wilkes, 2002).

As a result, the hard segment (showing high glass transition temperature, T_g) is mainly composed of isocyanates (such as TDI) bonded through urea linkages and the soft segment (low T_g), of flexible polyol chains. The urethane linkages (formed during the gel reaction) covalently bond these two segments and correspond to the chemical crosslink of PUR flexible foams (Fig. 1.4).

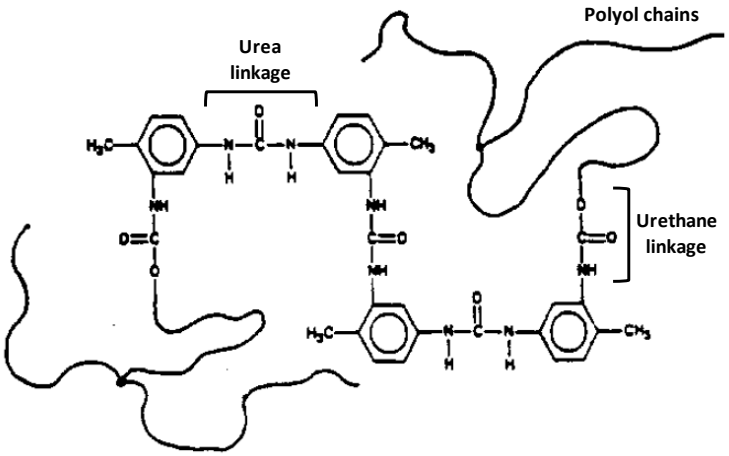


Figure 1.4 Covalent network structure of PUR flexible foams (adapted from Herrington and Hock as cited in Dounis & Wilkes, 1997: 2821).

In general, the backbone of the polymer consists on TDI-urea hard segments connected to soft segments via urethane linkages (Thomas *et al*., 1994).

The typical segregation of polyurethane into a two-phase morphology (HS and SS) takes place because of thermodynamic incompatibilities between the two segments, strong hydrogen-bonding interactions (H-bonds) and excess of HS concentration (Thomas *et al*., 1994; Aneja & Wilkes, 2002). As a result, the hard segments precipitate and polyurea micro-domains are formed, which are called hard-domains. These hard-domains are thought to show some crystalline order (paracrystalline structures) because infrared studies have confirmed strong hydrogen-bonding interactions between them (Merten *et al*., 1968; Priester *et al*., 1990). Moreover, based on TEM, SAXS and WAXS studies, they are thought to show structures c. 10 nm wide by 50–300 nm long (Armistead *et al.*, 1988; Kaushiva & Wilkes, 2000). Besides the presence of these micro-domains, larger scale structures have also been identified on PUR flexible foams. These are called 'urea balls' or 'urea aggregates', which are c. 0.3 μm wide by 100–400 nm long (depending on hard segment content) (Bailey & Critchfield, 1981; Armistead *et al.,* 1988) and a lamellarlike structure (Moreland *et al.*, 1991). Although until 2002 the chemical nature of these aggregates was not known, a study conducted by Rightor *et al*. (2002) using scanning transmission X-ray microscopy has proved that TDI-urea is the main constituent of these macrophase precipitates. It also proved that the amount of polyol is higher in the matrix than in the precipitates. To summarise the information presented above, a schematic representation of a possible PUR flexible foam morphology is shown in Fig. 1.5, as proposed by Moreland *et al*. (1991).

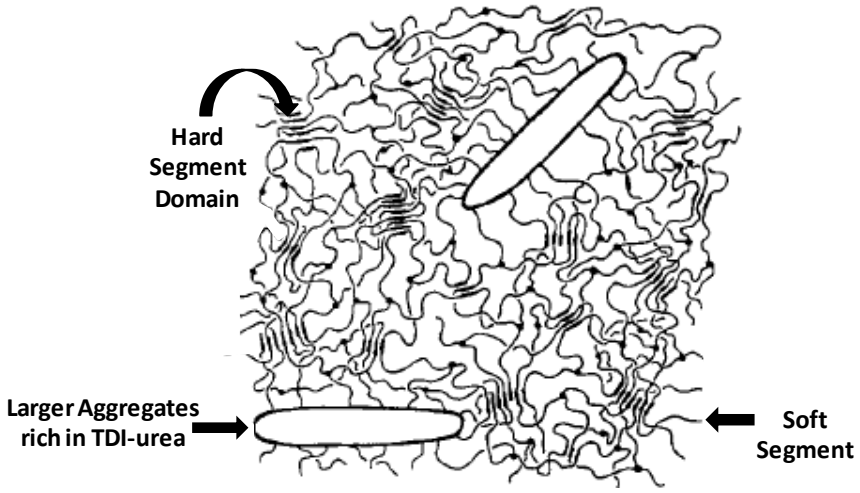


Figure 1.5 Schematic morphological model for PUR flexible foams (not shown to scale) (adapted from Moreland *et al.*, 1991: 811).

From this model, the importance of hydrogen-bonding interactions between HS chains is shown, resulting in the formation of the segregated structure divided into hard-domains (micro- and larger

aggregates) and soft-domains. These interactions not only consist of the physical crosslink of PUR flexible foams (Priester *et al*., 1990; Thomas *et al*., 1994), but also 'act like "covalent crosslinks" at room temperature' (Thomas *et al*., 1994: 2156). Therefore, their crucial role in the design of a PUR segregated morphology is frequently stressed in the literature as well as their decisive role in the physical and chemical properties of the final material. Since these bonds could be particularly important in the long-term stability of polyurethane, a deeper insight into these interactions is discussed hereinafter and in Chapters 3 and 4.

Regarding the importance of hydrogen-bonding interactions, infrared spectroscopy has commonly been applied for the characterisation of H-bonds between both hard-hard and hard-soft segments (Priester *et al*., 1990; Moreland *et al.,* 1991; Thomas *et al.*, 1994). Moreover, some authors have been focusing on the establishment of these bonds during the development of the PUR foam 3D structure using forced-adiabatic conditions and time-resolved FTIR spectroscopy (Elwell *et al*., 1996). From these studies, important conclusions have been made. By following the carbonyl region absorptions (1800–1600 cm^{-1}), in the beginning of the reaction both urethane (–NH–COO– at c. 1730 cm^{-1}, assigned to non-associated urethane, i.e., free of hydrogen-bonding) and soluble urea (–NH–CO–NH– at c. 1715 cm^{-1}, assigned to non-associated urea) are detected (Fig. 1.6) (Priester *et al*., 1990; Elwell *et al.*, 1996). After a few minutes of the foam mixing, a band at c. 1640 cm^{-1} starts to appear which corresponds to the formation of associated (hydrogen-bonded) urea (Priester *et al*., 1990; Elwell *et al.*, 1996). This band is assigned to bidentate urea and suggests the presence of the previously mentioned ordered structure of the hard segment (paracrystalline) (Fig. 1.6).

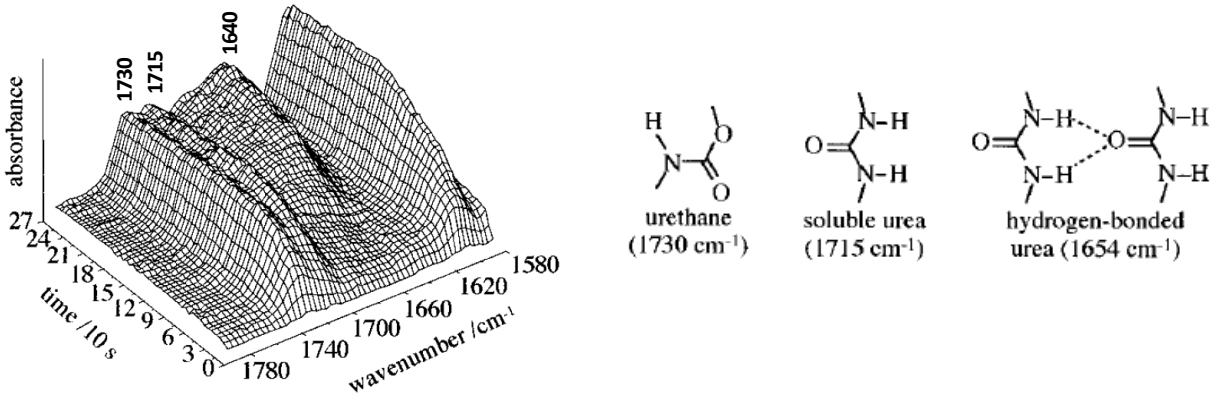


Figure 1.6 Three-dimensional surface plot of absorbance versus frequency, versus time for the carbonyl region of a PUR flexible foam. Urethane, soluble urea and hydrogen-bonded urea structures and absorptions are indicated (adapted from Elwell *et al.*, 1996: 2962).

The formation of monodentate urea has been assigned to bands between 1650–1680 cm^{-1}, suggesting the presence of a less ordered structure, especially found in the spectra of moulded foams [11] (Thomas *et al*., 1994). The assignment of the most important urea, urethane and H-bonds absorption frequencies involved in PUR structure is summarised in Table 1.1 (Yilgör *et al*., 2015: A26).

Table 1.1 Most important urea, urethane and H-bonds absorption frequencies involved in PUR structure (adapted from Yilgör *et al*., 2015: A26)

Group	Mode	Frequency (cm^{-1})
N-H	Free	3445–3450
	N–H ····· N–H	3315–3340
	N–H ····· O (ether)	3260–3290
C=O (urethane)	Free	1730–1740
	C=O ····· H–N	1700–1715
C=O (urea)	Free	1690–1715
	C=O ····· H–N	1650–1680 (disordered, monodentate)
	C=O ····· H–N	1630–1645 (ordered, bidentate)
N-H-C=O	Amide II	1540–1560

In addition, some authors focused on the weathering stability of these bonds (Moreland *et al*., 1994a, 1994b; Dounis & Wilkes, 1997; Boubakri *et al.,* 2009). Since their studies describe H-bonds in PUR flexible foams as labile to elevated T and RH (possibly affecting the lifespan of these materials), these results are discussed in the section dedicated to the deterioration of polyurethane (p. 33). In PUR moulded foams, H-bonds were concluded as more prone to ageing than in slabstock foams (Dounis & Wilkes, 1997). Therefore, to understand which differences are involved in this process, the manufacture of moulded foams is discussed hereinafter.

At first, the main clear difference between moulded and slabstock foams is their physical appearance. Whereas moulded foams show high density foam skins (which corresponds to the superficial area in contact with the mould walls) and low-density foam cores, slabstock foams show uniform porous cross sections (Ashida, 1995b). However, additional and significant differences were found in the chemical composition of the two formulations. According to the cited literature, these differences affect the final properties and morphology of the polymer (Dounis & Wilkes, 1997; Kaushiva & Wilkes, 2000; Kaushiva *et al*., 2000). The main reason for this could be related to the technical requirements involved in the production of moulded objects. According to Kaushiva and Wilkes, the 'formulations are optimized to obtain the lowest mold residence times possible while still achieving the desired

[11] Moulded foams are discussed later in this section.

performance in tests such as compressive load bearing and resiliency' (Kaushiva & Wilkes, 2000: 6981). Therefore, these differences are summarised in Table 1.2, and discussed in the following paragraphs.

Table 1.2 General differences between slabstock and moulded PUR flexible foams formulation and morphology (commonly mentioned in the accessed literature)

	Slabstock PUR Flexible Foams	**Moulded PUR Flexible Foams**	**Reference**
Diisocyanate	TDI	TDI or blends of TDI with polymeric isocyanates	(Dounis & Wilkes, 1997)
Polyol	Polyether triols with 3000–4000 Mw Lower EO content and high content of secondary OH endgroups	Polyether triols with 4000–6000 Mw Higher EO content (c. 17% ethylene oxide capped polyether triol) and high content of primary OH (in the range of 65–90%) Or The so-called 'graft copolymer polyol' in foam formulation	(Saunders & Frisch, 1962; Thomas *et al*., 1994; Dounis & Wilkes, 1997; Zhang *et al*., 1998; Kaushiva *et al*., 2000; Li *et al*., 2002)
Catalysts (or cross-linking agents)	Tin and amine catalysts such as DABCO 33LV	Amine catalysts such as MbOCA or DEOA	(Zhang *et al*., 1998; Thomas *et al*., 1994; Dounis & Wilkes, 1997; Moreland & Wilkes, 1991)
Additional additives to improve indentation load deflection	Not required Good hardness without any extra additives	Polymeric polyols	(Saunders & Frisch, 1962; Dounis & Wilkes, 1997; Zhang *et al*., 1998)
Polymerisation Reactions	Gelling reaction rate much slower than blowing reaction rate	Gelling reaction rate closer to blowing reaction rate	(Zhang *et al*., 1998)
Morphology	**Hard Segment Micro domains**		(Dounis & Wilkes, 1997; Zhang *et al*., 1998)
	Long length and efficiently packed Higher level of bidentate urea (strong H-bonds within the HS)	Short length and weakly ordered In general, no bidentate urea but only monodentate urea (weaker H-bonds within the HS)	
	Hard Segment Macro domains		(Kaushiva *et al*., 2000)
	Commonly found	Absent (in general)	

Whereas it is common for both productions to use TDI-80, blends of TDI with polymeric MDI started to be used in cold-moulded[12] flexible foams in the 1960s (Freitag & Volland, 1985: 204). These blends have been preferably chosen given the benefit of low moulded and oven temperatures (Saunders & Frisch, 1962; Ashida, 1995b; 2007; Szycher, 2013). Regarding the choice of the polyol, although slabstock polyols show c. 3000–4000 Mw, typical moulded polyols show higher values, between 4000–6000 Mw (Kaushiva *et al*., 2000). Another difference resides in the ratio of ethylene oxide (EO) to propylene oxide (PO). Slabstock foams made use of lower EO contents (or none) and high ratios of secondary OH endgroups, while moulded foams use higher EO contents and higher ratios of primary O–H endgroups (Herrington & Hock, 1997 as cited in Kaushiva *et al*., 2000). Justifying this choice is the requisite of high polymerisation rates in moulded foam products (Li *et al*., 2002; Dounis & Wilkes, 1997). Thus, highly reactive polyols are used, the thermodynamic incompatibility between water and other components is changed, and the solubility between HS and SS domains is altered (Kaushiva & Wilkes, 2000: 6984). Another difference is the addition of crosslinking agents in moulded foams (Kaushiva & Wilkes, 2000). For that, amine additives have been commonly used and both diethanolamine (DEOA) (Fig. 1.7, on the left) (Kaushiva & Wilkes, 2000) and 4,4'-methylene-bis(2-chloroaniline) (MbOCA) (Fig. 1.7, on the right) (Zhang *et al*., 1998) were found to be frequently mentioned in polyurethane patents from the 1960s and 1970s (von Benin & Piechota, 1967; Wolff & Larsen, 1972; Sundholm, 1973; Taub, 1974). Both additives show low reactivity rates (which allows an efficient link to the foam network to form) and aim to make foam flow and mould filling easier, without disregarding good compression set properties (Zhang *et al*., 1998). Nevertheless, important differences in the final polymer morphology have been reported concerning the use of DEOA or MbOCA (Thomas *et al*., 1994; Dounis & Wilkes, 1997; Zhang *et al*., 1998; Kaushiva & Wilkes, 2000; Li *et al*., 2002; Aneja *et al*., 2003; Lan *et al*., 2014).

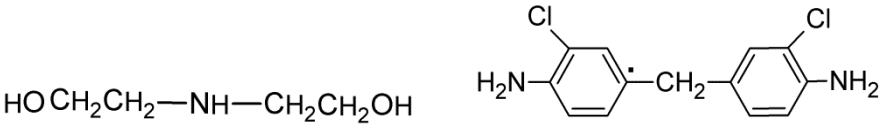


Figure 1.7 Examples of chain extenders used in the production of moulded foams. Left: diethanolamine (DEOA). Right: 4,4'-methylene-bis(2-chloroaniline) (MbOCA). (Zhang *et al*., 1998: 330)

As stated by Zhang and co-authors, DEOA 'can form two urethane foam linkages which are similar to the product between polyol and isocyanate' (Zhang *et al*., 1998: 340). Consequently, these urethane-forming groups (O–H groups of DEOA) will improve the chemical compatibility between hard and soft

[12] Within moulded foams, hot and cold processes can be found.

segments, 'disrupt the urea microphase separation' and eliminate the formation of bidentate urea (Zhang *et al*., 1998: 348). Moreover, when DEOA is added, the HS micro domains become smaller (c. 5 nm in diameter) and the formation of larger scale aggregates has not been identified (Dounis & Wilkes, 1997; Kaushiva & Wilkes, 2000). This has also been confirmed from infrared studies (Fig. 1.8) (Dounis & Wilkes, 1997). Instead of the bidentate urea band at 1640 cm^{-1} (as displayed by slabstock foams), moulded foams spectra show monodentate urea absorptions between 1680–1650 cm^{-1} and free urea at 1715 cm^{-1} (Dounis & Wilkes, 1997; Li *et al*., 2002). AFM and SAXS studies have also confirmed this tendency (Kaushiva & Wilkes, 2000; Li *et al*., 2002).

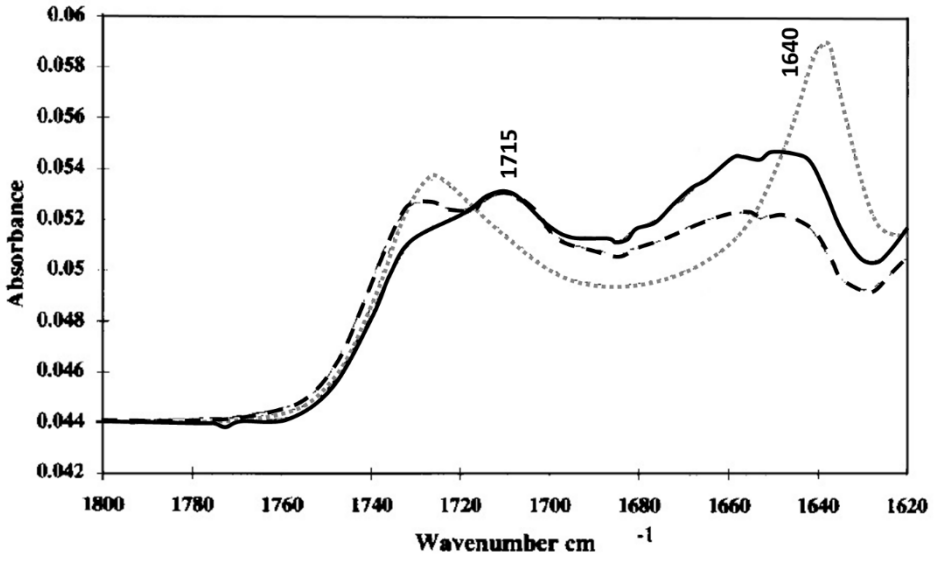


Figure 1.8 Differences in the C=O region of infrared spectra of moulded (black) and slabstock foams (grey). Black spectra correspond to PUR moulded foams with high (solid line) and low (dash line) hard segment content (adapted from Dounis & Wilkes, 1997: 2827).

On the other hand, the use of MbOCA (instead of DEOA) results in different spectral variations. According to Zhang *et al*.'s study, not only the bidentate urea band was still detectable at 1640 cm^{-1} (although with lower intensity than slabstock foams spectra), as its broadening was observed (in comparison to moulded foams with DEOA or with no additives) (Zhang *et al*., 1998: 348). As a possible reason, the absence of hydroxyl groups on the MbOCA structure (Fig. 1.7) can be named. Therefore, the improved phase mixing achieved by DEOA does not occur to the same extent as with MbOCA. However, no further infrared studies focused on the implications of MbOCA on the morphology of PUR moulded foams have been found. This can be explained by the classification of this additive as carcinogen by the Federal Register (journal of the U.S. Government) in 1973 (Federal Register as cited in Graefe *et al.*, 1975: n.p.), leading to its prohibited use in certain countries (e.g. USA).

In summary, moulded foam differs from slabstock foam formulations in the use of reactive polyols and crosslinking agents, which at the end, result in short and less ordered HS domains. Consequently, the weakened system of H-bonds makes these foams more prone to deterioration than slabstock foams. Since this could have significant implications in the current preservation condition of PUR moulded foam case studies from the MUDE collection, this subject has been considered in depth in the research presented in Chapters 3 and 4.

Nonetheless, the MUDE collection shows other forms of polyurethane. For instance, films and coatings are commonly found in artificial leathers from fashion garments and accessories. Due to their importance in the collection and the presence of case studies already showing deterioration, these materials are discussed here as part of the polyurethane class known as TPU. According to the 'Polymer Technology Dictionary' (1994) by T. Whelan, TPU (or TPE-U) is an abbreviation for *thermoplastic polyurethane* (Whelan, 1994: 452), but is also known as a *thermoplastic elastomer - urethane based* or as, *thermoplastic urethane elastomer* or as *linear PU* (Whelan, 1994: 441). In this class, polyurethane polymers such as films and coatings are of particular importance in fashion industries due to their possible use in leathers and textiles. According to Meckel *et al*., 'TPUs were the first polymeric materials to combine both rubber elasticity and thermoplastic characteristics' (Meckel *et al.*, 1996: 32). In fashion, these properties have been highly appreciated since they could offer the possibility of being highly elastic and at the same time, abrasion resistant. In addition, and like PUR foams, TPU films can also be tailor-made into desirable properties. Nevertheless, raw materials, polymerisation processes and morphologies are different and therefore, discussed hereinafter.

In general, diisocyanates, chain extenders (61–400 Mw), polyols (ester or ether-based, 600–4000 Mw) and additives (e.g. mould release agents, reinforce compounds and stabilisers) are the main raw materials of TPU films formulations (Meckel *et al.*, 1996: 17). From this, similarities with PUR flexible foams can be seen. The main difference resides in the average functionality of the starting materials. While in PUR foams the polyol functionality is close to 3 or higher (to obtain a 3D network) (Armistead *et al*., 1998); in TPU films, the functionality is close to 2, and linear polyurethanes are produced (Meckel *et al.*, 1996). As stated by Meckel *et al.*, 'This insures formation of high molecular weight linear chains with no or only very few branch points' (Schollenberger & Dinbergs, 1979 as cited in Meckel *et al.*, 1996: 17). C. Hepburn in her publication, 'Polyurethane Elastomers', presented a scheme illustrating the structure-property relationships in polyurethanes according to their degree of branching or crosslinking and crystallinity (Fig. 1.9) (Hepburn, 1992: 2). From this figure, the unlimited variety of materials offered by polyurethanes is evident, even within the class of TPUs. TPUs are segmented structures comprising hard and soft segments 'chemically linked together along a macromolecular backbone', as shown in Fig. 1.10 (Yilgör *et al*., 2015: A1). Depending on the choice of the diisocyanate, chain extender and polyol, hardness grades ranging from 78 Shore A to 74 Shore D can be offered by

TPUs (Whelan, 1994) and with that, 'soft flexible, elastomeric materials' or 'more brittle, high-modulus plastics' are produced (Meckel *et al.*, 1996: 18). In here, the production of films and coatings from TPUs will be mainly discussed.

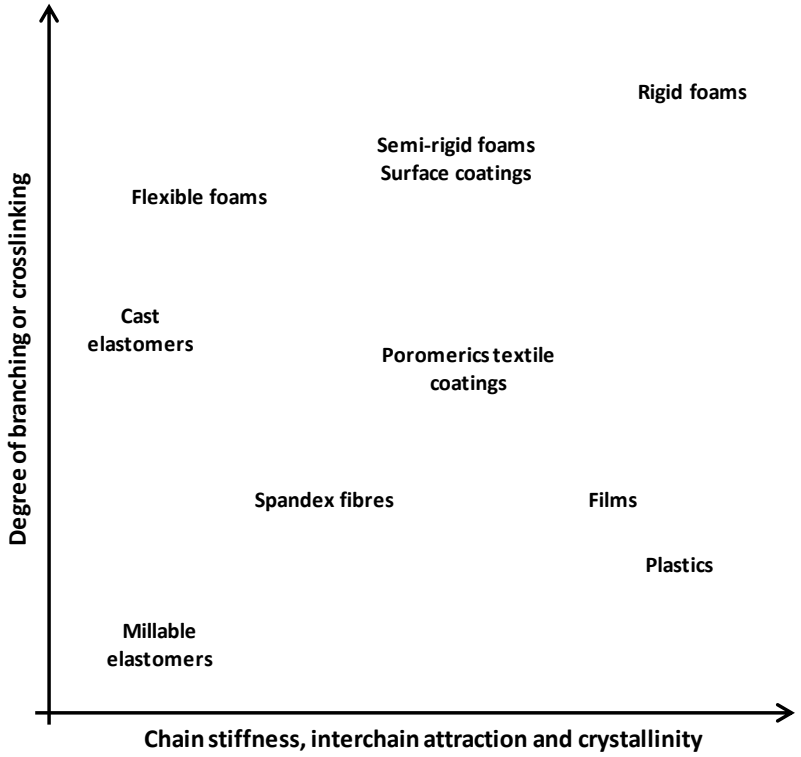


Figure 1.9 Structure-property relationships in polyurethanes (adapted from Hepburn, 1992: 2).

Figure 1.10 Schematic representation of a segmented TPU: diisocyanate (●) and chain extender (□) (adapted from Yilgör *et al*., 2015: A1).

For the polyol, hydroxyl terminated polyester made from adipic acid and excess of glycol; or hydroxyl terminated polyether produced from poly(oxypropylene) glycols (PPG) or poly(oxytetramethylene) glycols (PTMG, PTMO) have been used (Saunders & Frisch, 1962; Meckel *et al.*, 1996: 18); and for the diisocyanate, 4,4'-diphenylmmethane diisocyanate (MDI) (Fig. 1.11) has been the most preferred choice (Saunders & Frisch, 1962; Meckel *et al.*, 1996: 21).

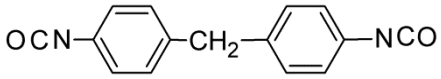


Figure 1.11 4,4'-diphenylmethane diisocyanate (MDI).

In addition, chain extenders are also used, which could be diamines or diols (Yilgör *et al*., 2015). The choice of the diisocyanate along with the chain extender is commonly mentioned to be of particular importance in the design of TPUs since they determine the HS and the final physical properties of the material (such as hardness) (Meckel *et al.*, 1996: 21). For that, linear diols (chain extenders) such as 1,4-butanediol (BD) (Fig. 1.12) have commonly been applied (Meckel *et al.*, 1996), which result in the formation of urethane linkages. In PUR flexible foams, water can be addressed as the chain extender, which at the end, results in the formation of urea linkages (Herrington & Hock, 1991 as cited in Yilgör *et al*., 2015: A7). TPU based films composed of MDI, BD and polyether or polyester macroglycols are particularly important in the market (Pompe *et al*., 1998).

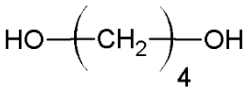


Figure 1.12 1,4-butanediol (BD).

In relation to the morphology of TPU films, similarities with PUR foams have been found in the literature (Meckel *et al.*, 1996). Both TPU films and PUR foams show a phase separated morphology (SS and HS) and two types of crosslink (chemical and physical). Nevertheless, whereas HS in PUR foams are mainly composed of TDI bonded through urea linkages and include strongly hydrogen-bonded urea, in TPU films, HS chains are generally composed of MDI bonded to linear glycols (chain extender) through urethane linkages and include strongly hydrogen-bonded urethane (Yilgör *et al*., 2015). On the other hand, phase separation is not complete in TPUs and soft segment phases can show a certain amount of hard segments, called residual or amorphous HS (van Bogart *et al.*, 1983; Harros *et al.,* 1989 and Li *et al*., 1992 as cited in Pompe *et al*., 1998). Similarly to PUR foams, due to thermodynamic incompatibilities between hard and soft segments, solubility parameters and formation of a hydrogen-bonded network (through urethane linkages), phase segregation takes places and ordered (crystalline) or semi-ordered (paracrystalline) structures of HS domains are formed (Meckel *et al.*, 1996; Hepburn, 1992). These domains are also called HS 'crystallites' (Frick & Rochman, 2004: 413), which, according to Briber and Thomas, can show (in some cases) two different morphologies: type I – related to a higher degree of phase mixing; and type II – related to stronger phase separation (Briber & Thomas, 1983 as cited in Frick & Rochman, 2004: 414). In general, 'The hard segments act as multifunctional tie

points functioning both as physical crosslinks and reinforcing fillers, while the soft segments form an elastomer matrix which accounts for the elastic properties of TPU' (Frick & Rochman, 2004: 413). The HS domains in TPUs are thought to show similar sizes with the smaller HS domains found in PUR foams with comparable HS content (Moreland *et al.,* 1991; Armistead *et al.*, 1988; Kaushiva & Wilkes, 2000), i.e., c. 50 nm wide by 100–400 nm long according to Zheng and co-authors (Zheng *et al*., 2005 as cited in Voda *et al*., 2006: 4808). However, in TPU films, larger aggregates as shown by PUR foams have not been found (Yilgör *et al*., 2015). Even so, according to Aneja and Wilkes, superstructures showing c. 5–15 nm were observed, and if the HS possesses suitable symmetry, 'spherulitic texture' structures are possible (Aneja & Wilkes, 2003). As stated by Yilgör *et al*., 'the degree of microphase separation, microphase morphology and domain sizes varied greatly depending on the soft segment structure and solubility parameter and the hard segment content of the TPUs' (Yilgör *et al*., 2015: A14–15). In TPU films there is no covalent network but a linear segmented system, i.e., TPUs 'are linear multiblock copolymers containing soft and hard segments' (Pompe *et al*., 1998: 5147). According to Armistead *et al*., this 'influences the long-term creep, stress relaxation, and level of extensibility' (Armistead *et al,* 1998 as cited in Moreland *et al.,* 1991: 802), and therefore, higher elongations are allowed. Thus, the morphology between PUR foams and TPU films (at room T) is different, as proposed by Lee *et al*. (Lee *et al*., 1987) and shown in Fig. 1.13.

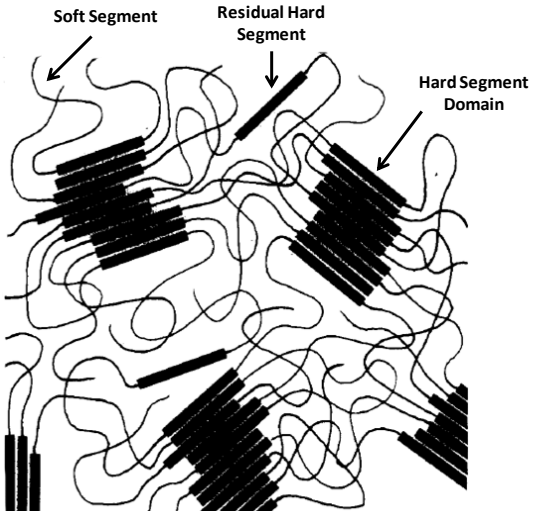


Figure 1.13 Schematic representation of a TPU morphology at room T (adapted from Lee *et al*., 1987: 2090).

The thermoplasticity of these materials results from the reversibility of the H-bonds (physical or pseudo-crosslinking). According to Hepburn, these physical forces 'are reversible with heat and with solvation, offering thermoplastic processing' (Hepburn, 1992: 245). This process, as proposed by Wilkes *et al*., (Wilkes *et al*., 1975) is shown in Fig. 1.14. Moreover, the common choice for diols instead

of diamines (as chain extenders) resides in lower values for the melting temperature of the HS. As previously mentioned, the reaction between an amine and an isocyanate leads to urea linkages and consequently, to strong hydrogen-bonded urea. According to Yilgör *et al.,* 'in strongly hydrogen bonded segmented polyureas, the high degree of cohesiveness due to the bidentate hydrogen bonding may limit their abilities to be melt processed (Yilgör *et al*., 2015: A29–30). Thus, diols are preferred.

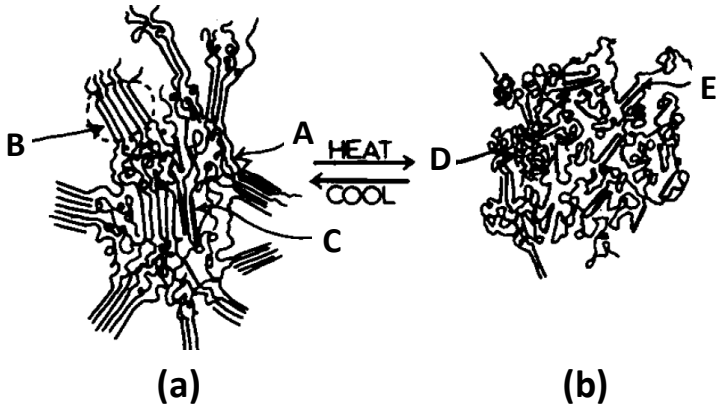


Figure 1.14 Schematic model depicting the morphology of a segmented TPU at both a) long time and b) following heat treatment: (A) partially extended soft segment, (B) hard segment domain, (C) hard segment, (D) coiled or "relaxed" soft segment, (E) hard segment domain with lower order (Wilkes *et al*., 1975: 324).

Regarding the manufacturing of TPUs, two types of procedures are generally found, the 'one shot' method and the 'prepolymer method' (Yilgör *et al*., 2015). The last one is the most preferably applied and consists of two steps (Yilgör *et al*., 2015). At first, the diisocyanate reacts with the polyol to form the isocyanate-terminated prepolymer; then, the chain extender (diol) is added, reacts with the prepolymer and the high-molecular-weight-segmented polyurethane is formed. The first reaction takes place in bulk (in general) and the second is 'usually conducted in a twin-screw extruder in melt, or in solution' (Yilgör *et al*., 2015: A6). According to the literature, 'This is due to very high viscosities reached as a result of the increasing molecular weight of the polymer and formation of strong hydrogen bonding between the urethane or urethaneurea hard segments formed' (Krol, 2007 as cited in Yilgör *et al*., 2015: A6). If the 'one-shot' method is used, a random distribution of the hard and soft segments is achieved; on the other hand, if the 'prepolymer' method is chosen, well-defined and homogenously distributed HS domains are obtained.

In terms of processing, typical methods for thermoplastic materials can be applied in TPUs. As examples, injection moulding, extrusion, blow molding, calendering and solution fabrication could be named (Meckel *et al.*, 1996; Hepburn, 1992). For fashion industry and especially, textile and leather industries, calendering, solution applications and reactive coatings are of particular importance. Within calendering, two important variations are commonly practised with TPU, namely hot-melt

calendering and film lamination (Hepburn, 1992). As stated by Wang *et al*., 'TPU films provide a softer 'feel' or drape than polyester, with better moisture vapor transmission rates' (Wang *et al*., 2005: 18). Moreover, since they are 'permeable to water vapor, or 'breathable', they are highly appreciated materials in clothing such as outerwear, sportswear, footwear and gloves (Wang *et al*., 2005: 18).
In conclusion, due to the unlimited chemical and physical versatility of PUR foams and TPU films, the knowledge about polyurethane polymer morphology is crucial for an understanding of its properties and its long-term behaviour. In conservation, this is particularly important for the definition of conditions and for the decision-making process involved in the establishment of preventive measures.

1.2. The deterioration of polyurethane

Polyurethane is known for its ephemeral nature and is placed in the range of the most difficult synthetic polymers to preserve (Kerr & Batcheller, 1993; Garside & Lovett, 2006; Shashoua, 2009b; Lattuati-Derieux *et al*., 2011; van Oosten, 2011; Lavédrine *et al*., 2012a; Pellizzi *et al*., 2014). The deterioration of polyurethane has been widely investigated (Kerr & Batcheller, 1993; Garside & Lovett, 2006; Lattuati-Derieux *et al*., 2011; Rychlý *et al*., 2011; Mitchell *et al*., 2013; Pellizzi *et al*., 2014; Sustar, 2014). Nevertheless, most of the research studies have been focused on polyurethane foams. As a reason, foams are particularly prone to deterioration due to their open-cell and porous structure (superior accessibility of oxygen, light and water), showing a lifespan of 20 to 50 years (Kerr & Batcheller, 1993; Garside & Lovett, 2006; Shashoua, 2009b; Lattuati-Derieux *et al*., 2011; van Oosten, 2011; Lavédrine *et al*., 2012a; Pellizzi *et al*., 2014). Apart from these factors, during industrial processing PUR foams are subjected to severe conditions that favour photo and thermal oxidation processes (Shashoua, 2009b). Consequently, the deterioration of PUR foams has been highly focused on conservation studies.
According to those studies, the ageing mechanisms are largely dependent on the compounds involved in polyurethane chemical structure. While ester-based susceptibility to hydrolysis and thermal ageing in humid conditions has been mentioned, ageing studies of ether-based polyurethanes have shown its susceptibility to photo-oxidation and resistance to hydrolysis (Kerr & Batcheller, 1993; Garside & Lovett, 2006; Lattuati-Derieux *et al*., 2011; Pellizzi *et al*., 2014). Nevertheless, authors such as Keneghan state that 'oxidation is the significant pathway for both groups' (Keneghan, 2003 as cited in Lovett & Eastop, 2004: 101) and Williams thought that 'polyether oxidation requires the presence of moisture' (Williams, 2003 as cited in Lovett & Eastop, 2004: 101).
For the assessment of the chemical and physical deterioration of polyurethane foams, several analytical methods have been used: Fourier transform infrared spectroscopy in attenuated total

reflection mode (FTIR-ATR) (Garside & Lovett, 2006; Kerr & Batcheller, 1993; Lattuati-Derieux *et al*., 2011; Lavédrine *et al.*, 2012a; Mitchell *et al.,* 2013; Pellizzi *et al*., 2014; Shashoua, 2009b; van Oosten, 2011), thermogravimetry (TG) and differential scanning calorimetry (DSC) (Pellizzi, *et al*., 2014; Rychlý, *et al*., 2011), mechanical tests (Garside & Lovett, 2006; Pellizi, *et al*., 2014; van Oosten, 2011) and also, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and headspace-solid phase microextraction coupled with gas chromatography and mass spectrometry (HS-SPME-GC/MS) (Lattuati-Derieux *et al.,* 2011). Curiously, and to our knowledge, there are no publications concerning the use of Raman microscopy for the assessment of PUR deterioration, even though it has been proved to be a valuable technique for the study of C–C and C=C stretching vibrations, polymer conformational structures and to characterise hydrogen-bonding interactions on plastics and synthetic polymers (Edwards *et al*., 1993; Chalmers & Everall, 1999; Miller *et al*., 1990; Lee, 1997; Lewis *et al*., 2014).

Nevertheless, from the references cited above, important conclusions have already been published. The photo-degradation of ether-based polyurethane foams based on aromatic diisocyanates is initiated at the methylene group ($C–H_2$) between aromatic rings of methylene diphenyl diisocyanate (MDI) and involves two different mechanisms (Wilhelm *et al*., 1998). The first is the formation of quinoid-type products by hydrogen abstraction and oxygen addition giving rise to discoloration; the second is a photo-Fries reaction which results in the formation of peroxides that absorb in the range of 300nm–400nm (Gardette & Lemaire, 1981; Kerr & Batcheller, 1993; Wilhelm *et al*., 1998). Based on a previous infrared spectroscopy study on the photochemical degradation of an ether-based polyol, it has been concluded that the extreme photochemical sensitivity of the soft segment (ether-based) leads to the formation of hydroperoxides and consequently, to formates (main photoproduct), esters and hemiacetals as well as to alcohols and carboxylic acids (Gardette & Lemaire, 1981; Wilhelm & Gardette, 1998). Furthermore, and according to the analysis of the volatile compounds by HS-SPME-GC/MS, the photo-oxidation ageing of polyether-based PUR foams leads to the formation of glycol derivatives (Lattuati-Derieux *et al*., 2011). Thus, solid and volatile products of artificially aged ether-based PUR foams have been characterised and both approaches confirmed the higher susceptibility of ether-based polyols to oxygen and light.

According to Wilhelm and Gardette, ester-based SS 'present a weak reactivity in terms of photooxidation, (...) however, worth note that the oxidation of the polyurethane component can in turn induce the oxidation of the polyester soft segments' (Wilhelm & Gardette, 1998: 1232). From the photo-oxidation ageing experiment of a polyurethane based on polytetramethylene adipate glycol and MDI, carboxylic acids were detected as deterioration products (Wilhelm & Gardette, 1998). On the other hand, hydrolytic ageing studies for ester-based PUR foams confirmed the high susceptibility of ester-based SS to humid conditions and the formation of alcohol and acid raw products (e.g. adipic acid) as deterioration products (Pellizzi *et al*., 2014, 2016; Rychlý *et al*., 2011; Lattuati-Derieux *et al*.,

2011). However, none of these studies focused on the possible deterioration of hydrogen-bonding interactions within the polyurethane segregated structure as consequence of natural ageing processes. Since these bonds were described as particularly important in the establishment of the polymer final chemical and physical properties, additional studies were sought in order to deepen the knowledge on this subject. For that, the research work already conducted by chemists such as Moreland, Dounis and Wilkes was crucial (Moreland *et al*., 1994a, 1994b; Dounis & Wilkes, 1997).

In these studies, the authors have focused on the influence of relative humidity and temperature in the viscoelastic behaviour and compression set properties of PUR foams. Moreover, one of these studies compared moulded and slabstock foams (Dounis & Wilkes, 1997). Mechanical tests under different values of RH and T, and FTIR thermal analysis have suggested that the presence of humidity replaces some H-bonds for water molecules (Moreland *et al*., 1994a, 1994b). A recent study by Boubakri *et al.* has confirmed that water decreased the mechanical cohesion of a urethane-based thermoplastic elastomer (TPU) by destroying the polymer secondary links by water molecule diffusion (Boubakri *et al.,* 2009: 3963). The increase of temperature from 25°C to 100°C is also thought to disrupt the H-bonds in the HS, degrading both urea and urethane bonds (Moreland *et al.,* 1994a, 1994b). Therefore, since 'polyurethanes are strongly self-associated through intermolecular hydrogen bonding' (Coleman *et al.,* 1988: 60) and these bonds are labile at elevated T and RH, their possible role in the short lifespan of these materials was considered. According to a study by Dounis and Wilkes, this fact might be especially true in moulded foam objects. As stated by the authors, 'high temperatures and humidities 'plasticized' the moulded foams to a greater extent than the slabstock foams' (Dounis & Wilkes, 1997: 2819). As a reason for this, the authors pointed out the less ordered structure of the hard-domains on moulded PUR foams (Dounis & Wilkes, 1997). Once more, the knowledge about polyurethane morphology stands out as a crucial area for the understanding of the long-term behaviour of these materials.

1.3. Active and preventive conservation for polyurethane – a brief summary

Although polyurethane can be found in museum collections in the form of foams, films, coatings, fibres, adhesives and solids (among others), active conservation studies have mostly been focused on foams, in particular, on consolidation studies for flexible foams. The presence of 'loss of resilience, cracking and powdering' in a short time has been generally the main reason for the focus of conservation studies on this goal (van Oosten, 2011: 47). As explained before, foams are particularly prone to deterioration, showing a short lifespan. A literature review regarding PUR foams consolidation has already been published by Thea van Oosten (van Oosten, 2011). Therefore, only main

conclusions are briefly highlighted in this section, as well as the recent advances up to 2016, along with the active treatments for other forms of polyurethane.

In relation to foams, active conservation treatments started in the early 1990s with David Grattan (van Oosten, 2011). Since then and up to 2009, T. van Oosten identified 16 studies focusing on cleaning, consolidation, filling and/or adhesion procedures, mostly for ether-based polyurethane foams (van Oosten, 2011). The main goal of these studies was to maintain an object's shape and/or to avoid the complete loss of an object. In summary, van Oosten and A. Lorne identified *Impranil DLV*[13] (Bayer) as the best consolidant for ether-based PUR foams (2002), and the profit addition of *Vitamin E* as an anti-oxidant (2004) (van Oosten, 2011). In 2005–2006, the addition of *Tinuvin B75*[14] (Ciba-Geigy) to *Impranil® DLV* was also tested, resulting in advantageous results for ether-based polyurethane foams. From this formulation, a light-stabilising system was created and the proposed solution (5% *Tinuvin® B75* + *Impranil® DLV* in isopropanol/water) combined consolidation and protection against photo-oxidation, in a single application. Nevertheless, up to 2011, no consolidation treatment for ester-based polyurethane foams was developed (van Oosten, 2011). As part of the European *POPART* project (2008–2011), an in-deepth investigation into possible consolidants for this type of foams was carried out resulting in the benefit use of aminoalkylalkoxysilane (AAAS)-based treatments to reinforce unaged and artificially aged PUR foams (ester-based) (Pellizzi *et al*., 2016). From the recent study of Pellizzi *et al.,* the particular use of DIAMINO[15] (Abcr GmbH) solution at 2:5% in hexamethyldisiloxane (HMDS) was considered a 'valuable method to restore flexible degraded PUR ester foam mechanical properties and to extend the life of these kind of objects' (Pellizzi *et al*., 2016).

Active conservation treatments for polyurethane films and coatings (easily found in artificial leathers) are still lacking. Apart from the research study by the conservator Tim Bechthold, no more studies were found (Bechthold, 2006). In his research, consolidation and adhesion of polyester polyurethane coatings were studied in order to avoid the typical 'brittleness, cracking' and 'flaking' commonly found in objects showing these materials (Bechthold, 2006: 128, 131). For this purpose, the finely dispersed anionic polyurethane aqueous dispersion, *Isovin V* (Bayer) was tested, showing profitable results. Still, the author outlined the following, 'due to a lack of experience in conservation with these materials, there are no data available with regard to long-term behaviour for this kind of adhesive' (Bechthold, 2006: 132).

[13] Polyester/polyether-urethane dispersion of aliphatic isocyanate (van Oosten, 2011).

[14] Blend of three components: 20% *Irganox® 1135* (hindered phenolic primary antioxidant for processing and long-term thermal stabilization), 40% *Tinuvin® 571* (ultraviolet light absorber (UVA) of the hydroxyphenyl benzotriazole class) and 40% *Tinuvin® 765* (hindered amine light stabiliser, HALS) (van Oosten, 2011). In summary, *Tinuvin B75* prevents the processing, light and weather induced degradation of polyurethane products.

[15] N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane (Pellizzi *et al*., 2016).

For elastomeric polyurethane fibres and to our knowledge, no active conservation studies were found. This fact identifies the study of these materials as a high lacuna in PUR conservation research.

Regarding preventive conservation studies, it is well known that plastics deteriorate continuously and polyurethane, due to its inherent ephemeral nature is no exception. According to Yvonne Shashoua, 'prolonging the useful lifetime of plastics is possible today but is very limited in scope and effectiveness' (Shashoua, 2009a: 18). In this context, it has been stated since the late 1990s that ideally plastics 'should be stored in cold, dark, dry and oxygen-free conditions' (Williams, 1997: 2), and according to Shashoua, conditions such as c. 55% RH, T of 18 ± 2°C, no ultraviolet light, maximum illumination between 50–300 lux, and good ventilation have been adopted for the display of plastic objects (Shashoua, 2009b). However, even today, there are no established guidelines for plastics in museums and the mentioned conditions have been adapted from conservation guidelines of fragile materials[16]. Regarding PUR, with the exception of one preliminary study for ester-based PUR foams (Lovett & Eastop, 2004), there is no systematic research for the definition of environmental conditions for the storage of this polymer (Shashoua, 2009b). This fact was already highlighted by the European *POPART* project in 2012 as an urgent field of study (Rychlý & Rychly, 2012). For that purpose, the last chapter of this study is dedicated to the assessment of storage conditions for this highly ephemeral material based on natural ageing experiments in the dark for both unaged and pre-aged (c. 8–10 years) references. In these experiments, open-air and enclosed systems were assessed at room and low T, with and without oxygen.

1.4. The introduction of plastics in fashion and design – a brief summary

Before starting the discussion concerning the entrance of PUR polymers into the world of fashion and design, a brief summary focused on the introduction of plastics (i.e. synthetic polymers) in these two contexts should be given. Especially, because polyurethane was one of the most popular novelties of the design and fashion industry between the 1960s and 1970s and this period witnessed one of the highlighting moments of plastics production and consumption. The historical study of plastics (since the 1950s) has already been focused on by renowned authors such as Roland Barthes, Roger Lushington, Philip Ball, Susan Mossman, Stephen Fenichell, Sylvia Katz, Jeffrey L. Meikle, Jane Pavitt, Philippe Garner and Penny Sparke, among others. From their research, publications entitled 'Plastics and You' (Lushington, 1967), 'Classic Plastics, from Bakelite to High-Tech, with collector's guide' (Katz, 1988), 'The plastics age, from Bakelite to beanbags and beyond' (Sparke, 1993), 'American plastic, a

[16] According to Yvonne Shashoua, these guidelines have been traditionally adopted to preserve fragile materials (such as textiles and feathers) and for that reason, have been applied to plastics (Shashoua, 2009b: 195).

cultural history' (Meikle, 1995), 'Plastic. The making of a synthetic century' (Fenichell, 1997), and 'Early Plastics. Perspectives 1850-1950' (Mossman, 1997) are recognised as main references for this subject. To our knowledge, the particular use of polyurethane in fashion and design has not yet been the entire focus of a publication[17]. Nevertheless, on the previously mentioned literature, some notes concerning the importance and novelty of this material during the sixties and seventies have been found. One crucial example is the Roger Lushington's publication entitled, 'Plastics and You', resulting in one of the main sources for this section (Lushington, 1967). This book, written in the late 1960s by a former worker of Shell Chemicals, intended to 'stimulate a wider interest' on plastics (Lushington, 1967: back cover); as a result, valuable facts about polyurethane were found, especially concerning the decade where PUR chiefly became popular. Publications such as 'Italian Design: 1870 to the present' (Sparke, 1988), 'Sixties Design' (Garner, 1996), 'Fear and Fashion in the Cold War' (Pavitt, 2008), and 'An introduction to Design and Culture: 1900 to the present' (Sparke, 2013), were added to complement the information obtained. In general, this set of publications are focused on the history of plastics chemical development, on both economical and social contexts and, most importantly, on the material and immaterial values that cultural society found in plastics, and specifically, on polyurethane. Therefore, only the main points will be highlighted here to contextualise the subject.

There is no doubt that 'plastics are fascinating materials which have invaded every aspect of modern living' (Lushington, 1967: 11). This fascination was clearly stated by Roland Barthes in 1957, in his description of plastics as 'the stuff of alchemy' (Barthes, 1957/1991: 97). Furthermore, the author reported that testifying the production of a plastic was to testify a 'magical operation par excellence: the transmutation of matter' (Barthes, 1957/1991: 97). From this quote, we can imagine plastics as truly surprising materials for the public in the 1950s.

> *So, more than a substance, plastic is the very idea of its infinite transformation; as its everyday name indicates, it is ubiquity made visible. And it is this, in fact, which makes it a miraculous substance: a miracle is always a sudden transformation of nature* (Barthes, 1957/1991: 97).

The acceptance of plastics was difficult and still today, they are described as materials 'we love to hate' (Clough, n.d. as cited in Gross, 2012).

If we want to contextualise the 'Plastic Age' as once was the 'Stone Age', 'Bronze Age' and the 'Iron Age', according to R. Lushington, the 'Poly Era' started in the 1930s with the general use of 'poly'

[17] Regarding other plastics than polyurethane, some publications were found. As examples, celluloid was the main subject of R. Friedel publication 'Pioneer Plastic. The Making & Selling of Celluloid' (Friedel, 1983), nylon was studied by Susannah Handley in 'Nylon: The Story of a Fashion Revolution: A Celebration of Design from Art Silk to Nylon and Thinking Fibres' (Handley, 2000) and Tupperware was the focus of 'Tupperware: the promise of plastic in 1950s America' by Alison J. Clarke (Clarke, 1999).

materials (Lushington, 1967: 19). As stated by S. Katz and supported by S. Mossman, one of the reasons for this 'was that oil began to usurp coal's position as the source of the chemicals. This not only brought down the price of moulded end-products, but led directly to the development of new polymers' (Katz, 1988: 11; Mossman, 1997). The German chemist Hermann Staudinger also contributed to the increase of plastics chemical knowledge (Furukawa, 1998). By introducing the concept of the macromolecule in 1922, he 'completely changed the current theories about organic chemistry' and became known as the 'Father of Macromolecular Chemistry' (Katz, 1988: 11). From this moment, the public assisted to the appearance of many new plastics (Katz, 1988; Mossman, 1997).

As examples of popular plastics in the 1930s, polyamide fibres (known as nylon) by DuPont, polyethylene and poly(methyl metacrylate) (trade name 'Perspex') by ICI, polystyrene by I.G. Farben and poly(vinyl chloride) (PVC) by B.F. Goodrich Company can be named (Lushington, 1967; Katz, 1988; Mossman, 1997). As supported by S. Mossman and R. Newport, although these plastics were once restricted to high-technology purposes (transports, home appliances, military equipment, etc), they started to be commonly available for the consumer and soon gained a strong position in the market (Newport, 1993; Mossman, 1997). Polyurethanes, only commercially available in the 1940s from Bayer (at that time, still I.G. Farben) and DuPont, appeared in the market along with polyethylene terephthalate (trade name 'Terylene', by ICI), and soon became one of the most important novelties of the plastics industry (Lushington, 1967; Katz, 1988; Sparke, 1993). Silicones, urea- and melamine-formaldehydes and synthetic rubbers (as styrene-butadiene) were also part of the plastics market (Lushington, 1967; Katz, 1988). In the following decades (1950s and 1960s), a dramatic shift in both the economy and the chemical industry was registered, influencing the market of plastics in a positive way. For that, one of the most important contributions was the American funding implemented through the Marshall Plan, which financially supported European countries (Germany, Italy and Great Britain, among others) with the aim of assisting them in the resurrection from war destruction (Hogan, 1987 as cited in Sparke, 2013: 123). With this financing, the industry not only invested in the development of new polymers and new production processes, but started to promote its own products (plastics) in magazines, scientific journals, industrial plastic fairs and international exhibitions (Lushington, 1967; Sparke, 1993). These exhibitions took place both in Europe and in the USA. The 'Interplas' exhibition in London (1965) (Lushington, 1967: 102), DuPont's 'Wonderful World of Chemistry' show at the '1964–65 New York World's Fair' (Rhees, 2004 as cited in Ball, 2004: 663) and the Bayer 'Visiona'[18] pavilions in the Cologne Furniture Fairs (from 1968–1972) (Waentig, 2008b) are examples that can be named. As a result, plastics started gaining the trust of the public and the image

[18] From Bayer sponsorship and close relationship with highly known designers, polyurethane was one of the most important materials applied in 'Visiona' exhibitions. Given the importance of this event, this subject is explored in detail in Chapter 2.

of this new material improved. However, this was not a linear process and several drawbacks needed to be overcome (Manzini, 1993). In the research article, 'Material Doubts: The consequences of Plastic', J. L. Meikle focused upon the negative aspects related to the consumers' image of plastics, and more information on this subject could be accessed (Meikle, 1997).

Even so, further positive factors can be named and side by side with the industrial effort previously mentioned, space travel (first humans on the Moon in 1969) and the blockbusters of the sixties were mentioned in the literature as influences that helped to shift the image of plastics from poor materials to valuable media (Sparke, 2013). As examples of blockbusters from this period, 'Barbarella' (1968) and '2001: A Space Odyssey' (1968) can be named (Fenichell, 1997). With scenarios fully lined by synthetic films, foams and textiles and famous actors and actresses showing striking plastic outfits, the image of plastics gained popularity (Fenichell, 1997). Museums, in the same way, also began to promote plastic objects along with the concept of 'Good Design'. As examples, the Science Museum in London ran an exhibition in 1933 to promote popular plastics in the 1930s (Mossman, 1997) and the Museum of Modern Art (MoMA) in New York promoted the concept of good design with five exhibitions entitled 'What is Good Design', starting in 1950 (Sparke, 2013).

From this general context and as stated by Sylvia Katz, plastics were a new medium 'eagerly grabbed by designers' to 'express the new, informal, iconoclastic lifestyle' of the sixties (Katz, 1988: 13). Designers were particularly 'fascinated by the demands and opportunities of the new materials, and a great deal of design work has been done for innovative companies working with the best designers of the time' (Newport, 1993: 73). The motto 'Better Living Through Chemistry' gained a particular force during this period, which for DuPont was advantageously used to promote its materials (Fenichell, 1997: 234; Rhees, 2004 as cited in Ball, 2004: 663). After this, the public started to be invaded by plastic objects and daily life became marked by routines of plastic clothes, furniture, toys (Fig. 1.15), accessories and appliances.

> *Afterward, baby boomers played with Wham-O Hula hoops and frisbees, Barbie dolls and Revell airplane models, Lego blocks and Mattel machine guns. They ate breakfast at Formica dinettes, spilled milk from polyethylene tumblers onto vinyl floors, and left for school clutching disposable Bic pens. Their families experienced a proliferation of new plastic products -Tupperware, garbage pails and laundry baskets, Melamine dishes, appliance housings, Saran Wrap and dry cleaning bags, picnic coolers, scuff-proof luggage, Naugahyde furniture, Mylar recording tape, Corfam shoes, shrink-wrapped mats, Styrofoam egg cartons, artificial Christmas trees, and endlessly on* (Meikle, 1997: 278).

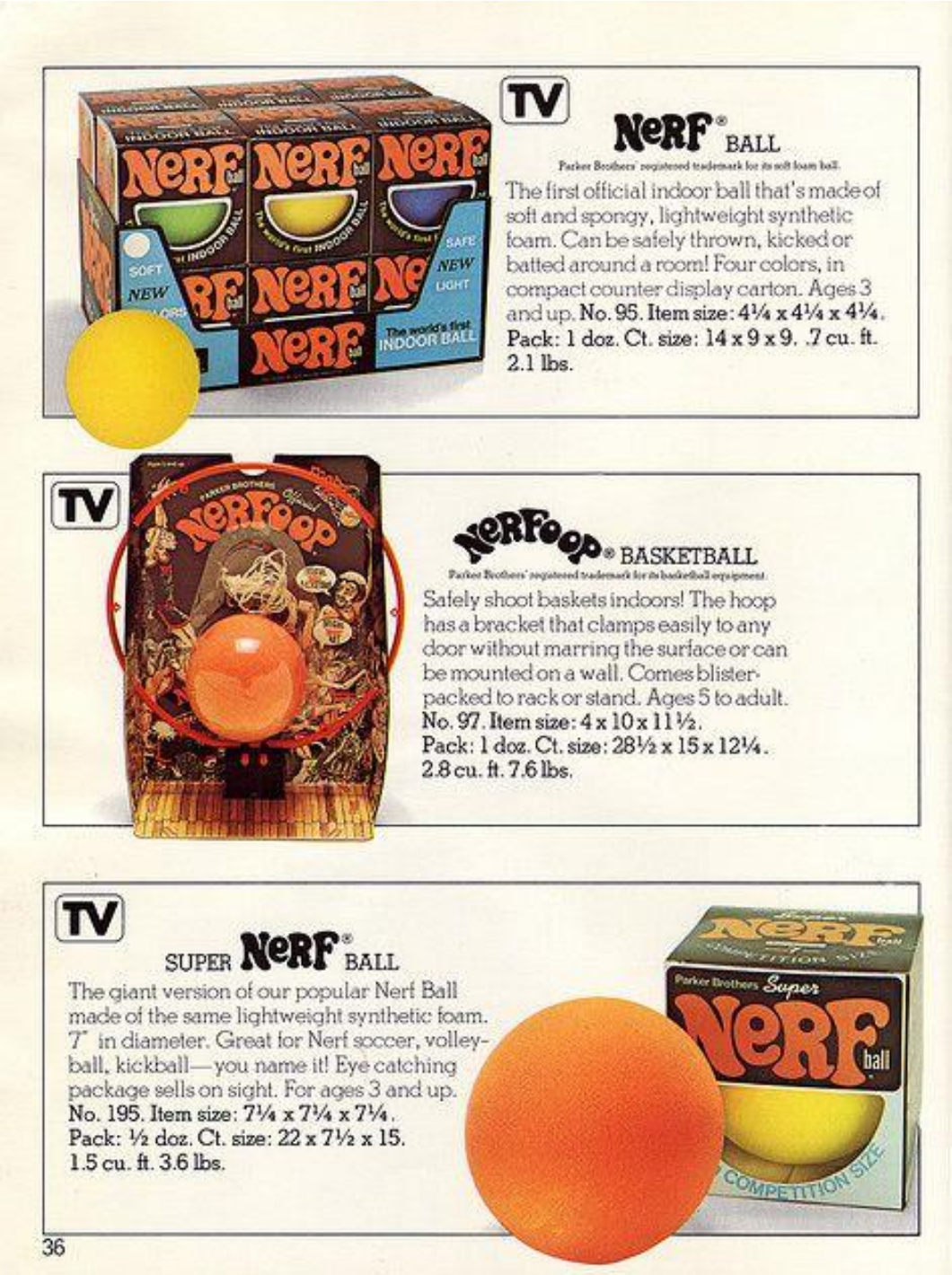


Figure 1.15 Parker Brothers, *Nerf* ball, 1970s, polyurethane foam. Catalogue of Parker Brothers from 1977 (Parker Brothers, 1977: 36).

Within the several areas of design, furniture design (specially, chairs) was foremost the major area to which plastics contribute to a higher extent in the 1960s (Lushington, 1967). In addition, and according to R. Lushington, from the whole set of synthetic materials, polyurethane 'has probably done more to revolutionize the furniture industry than any other plastic' (Lushington, 1967: 123).

1.4.1 Polyurethane in fashion and design

As supported by R. Lushington, PUR 'has become the most popular filling material for upholstered furniture, being tough, adaptable, and reasonably cheap', and able to substitute unsuitable foams 'which either lacked resilience or rapidly deteriorated in use' (Lushington, 1967: 123). Similarly, for Sylvia Katz, 'Expanded polyurethane foam, both flexible and rigid, freed furniture from the restriction of traditional construction' and the term 'fun foam furniture' was commonly mentioned to describe these objects (Katz, 1988: 13–14). One famous seat that illustrated the 'fun' character of polyurethane foam was the *Sea Urchin* chair (1968) designed by Roger Dean (Fig. 1.16) (Sparke, 1993).

Figure 1.16 Roger Dean, *Sea Urchin* chair, 1968, polyurethane foam (Sparke, 1993: 92).

Available by this date in varying degrees of rigidity, PUR was the ideal material for furniture (Sparke, 1993: 100). Furthermore, as supported by S. Katz and P. Sparke, two leading exponents of polyurethane furniture in the 1960s and 1970s were the Italian companies Gufram[19] and Poltronova. For example, the *Rocks* (1967) by Piero Gilardi (Gufram) and the *Superonda* (1966) by the radical group Archizoom (Poltronova) were mentioned as PUR foam objects illustrating the specific context and importance of Italian design during this period (Katz, 1988; Sparke, 1993: 100).

> *Foam chairs sprang up from prisons of flat, compressed envelopes; or the foam was simply wrapped around a sculptural metal frame. The development of soft and hard foams, with a simultaneously moulded protective skin, resulted in a rash of unusual, eccentric forms, such as the shapes produced by Gufram in 1969-70. Self-skinned foams masqueraded as grossly oversized blades of grass, prickly foam cactus hat stands, and boulders to be arranged casually in the home or garden* (Katz, 1988: 13–14).

> *Polyurethane foam, which can produce its own skin in a hot mould, will make sculptures that are also furniture: impossible, inhospitable shapes that nevertheless yield when you sit on them* (Katz, 1988: 114).

As defended by R. Newport and R. Lushington, most of this success came from collaborations between material manufacturers and furniture companies (Newport, 1997; Lushington, 1967). Bayer's work with notable designers such as Verner Panton, Olivier Mourgue and Joe Colombo (among others), are examples of that collaboration[20]. As mentioned by R. Newport, 'The profession of the industrial designer, then, was created to reestablish the vital connection between the end user and the manufacturer, and to create and develop products which satisfied both' (Newport, 1997: 73).

> *Nowadays, close liaison between furniture manufacturers and the foam producers ensures that there is a greater understanding of the importance of using the right density and type of foam for any particular application* (Lushington, 1967: 123).

Besides polyurethane, other plastics have also paved their way in this field. As examples, nitro-cellulose and polypropylene were also commonly used in furniture as lacquers and chair shells, respectively (Lushington, 1967: 123); PVC and rubber foams as upholstery materials; formica, addressed by S. Fenichell as 'The Surface with a Smile', as a popular plastic material in kitchens (Fenichell, 1997: 239); and finally, inflatable items made of PVC (Fenichell, 1997).

PVC, along with polyurethane had a tremendous success in the materialisation of what became known as the Pop culture (Sparke, 1993). In the words of Penny Sparke, these two plastics 'were the ideal

[19] The Italian companies Gufram and Poltronova have been explored in depth in the framework of this dissertation (Chapter 2).

[20] The relationship between furniture/design companies and manufacturer companies producing polyurethane polymers is discussed in more detail in the following chapter.

materials to represent several key Pop themes – among them a commitment to technology and the future: formlessness, flexibility, and softness' (Sparke, 1993: 94).

In fashion, clothes dependence on plastics was also clearly stated by Roger Lushington. In his words, 'It could be justifiably said that plastics have achieved their success in the clothing and footwear market by stealth' (Lushington, 1967: 131).

> *The very clothes we wear are becoming more and more dependent on plastics, either used on their own or in association with natural fibres. Those featherweight drip-dry underclothes, those soft hard-wearing jerseys, those sheer filmy stockings and fit-any-size socks, those smartly-cut non-crease suits and wipe-clean shoes all owe their very existence to plastics. Yes, undoubtedly we would miss them if they vanished!* (Lushington, 1967: 11).

PVC was highly used as a coating material for jackets, purses and shoes; and polyurethane, well known for its elastomeric fibres, was also known under the trade name *Spandex*. Nevertheless, plastics in fashion were not restricted to PVC and polyurethane, and nylon[21] was also a highly popular synthetic polymer in this period (Lushington, 1967; Fenichell, 1997; Sparke, 1993). Regarding polyurethane fibres, these filaments 'have remarkable stretch and recovery properties', 'can be used in swimsuits, foundation garments, and support hosiery, and will be increasingly used in stretch clothing of all sorts in the future' (Lushington, 1967: 131). Beside fibres, polyurethanes were also used in fashion items as foams, especially, for foam backed leathers that could be used to produce raincoats and overcoats (Lushington, 1967). As reported by Lushington, the major benefit of using polyurethane foam in these items was the better insulation efficiency without the addition of weight and the improved 'drape and feel of the coat' (Lushington, 1967: 131). Polyurethane leathers were also successfully used in the 1960s and 1970s. Corfam (Fig. 1.17), developed by DuPont, was an example of a popular polyurethane-based leather (Lushington, 1967). Corfam was a three-ply laminate synthetic leather composed of a polyurethane reinforced with polyester fibres base and a top coat of urethane copolymer, 'which gives a breathable micro-porous structure; hence the term 'poromeric' used to describe these materials' (Fenichell, 1997: 281; Lushington, 1967: 134). As stated by S. Fenichell, 'Corfam's vaunted superiority over leather was confirmed in a number of key areas: weight-up to a third less than its natural counterpart - moistureproofing, and of course, ease of maintenance' (Fenichell, 1997: 281). Another famous fashion hit of the sixties and seventies were the platform shoes (Fig. 1.18) where polyurethane soles were applied. In 1968, Bayer started to commercialise *Bayflex*™ and soon this material was highly used by the shoe industry (Schneider, 2013).

[21] Confirming this affirmation are the term 'nylo-mania' found in the literature (Fenichell, 1997: 226) and the existence of publications entirely (or sections) focused on this material, for example the book 'Nylon: the Man-made Fashion Revolution' by Susannah Handley (Sparke, 2013: 129).

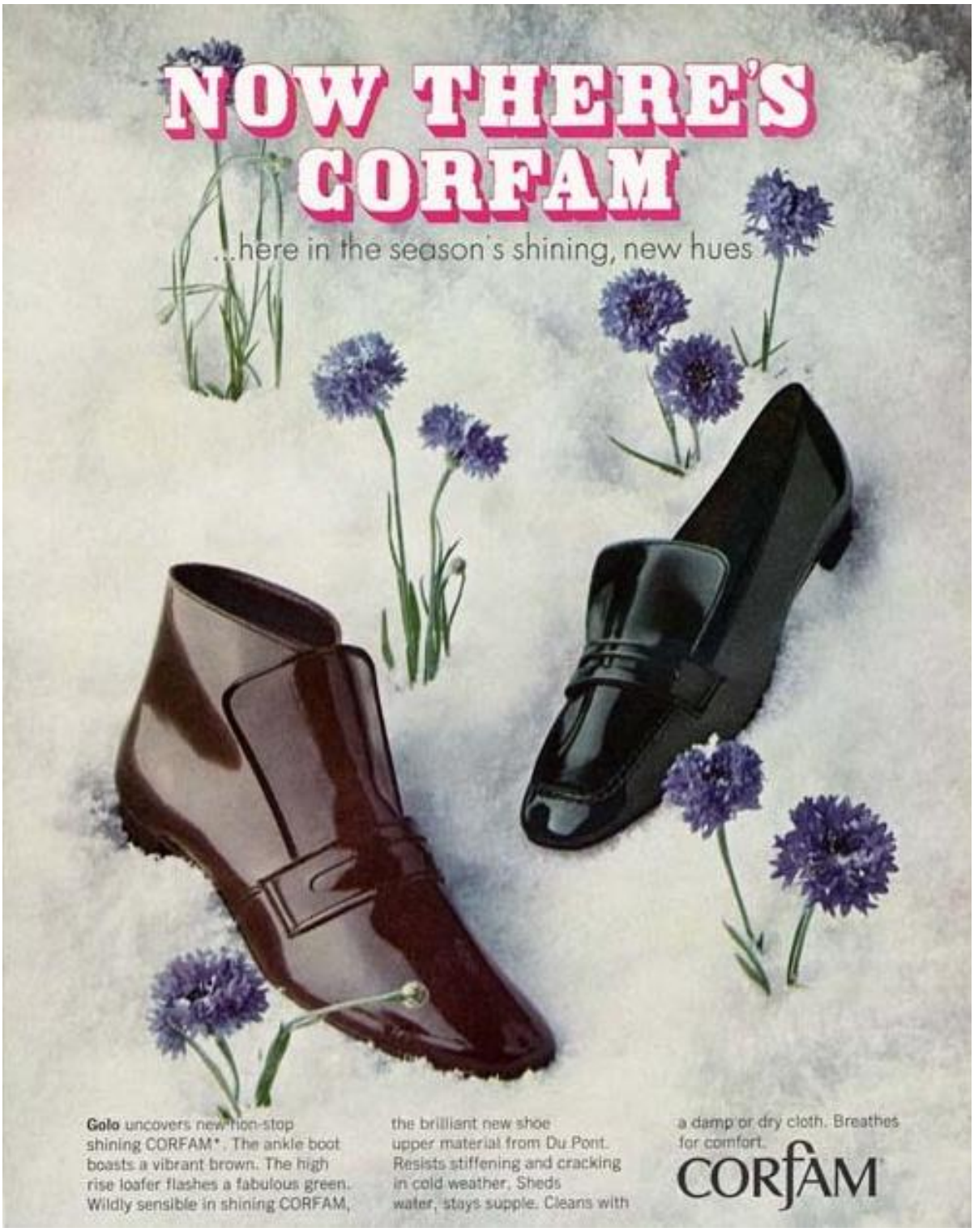


Figure 1.17 Corfam™ Ad from the 1960s (Conover, 2012).

The summer of love. Flower children. It is 1968, and young people are wearing long hair, brightly colored shirts and miniskirts. But the real hit of the season are shoes with platform soles. The chunky heel is made of wood or cork. Wood is heavy; cork is not resistant to abrasion. Bayflex™, a newly developed integral foam that, like all polyurethanes, would come to be used in a variety of applications, did not share these shortcomings. The foam and the strong outer layer were manufactured in a single processing step (Schneider, 2013: 56).

Figure 1.18 'ZOMP' shoes with polyurethane soles. Ad from the 1970s (Caldi, 1973: n.p.).

As examples of fashion designers who used plastics as fashion media in the 1960s and 1970s were André Courrèges, Paco Rabanne, Emilio Pucci and Pierre Cardin (Fenichell, 1997). Courrèges, in particular, made use of polyurethane artificial leathers in his collections from the 1960s and 1970s [22].

[22] The material characterisation of three case studies by André Courrèges and from the MUDE collection can be found in Chapter 3.

Overal, and as stated by Sylvia Katz, 'The sharp, shiny image of the 1960s was created entirely by synthetic plastics: wet-look polyurethane, glossy ABS, shiny, transparent acrylic and PVC (Katz, 1988: 14). Nevertheless, a drastic change in the image of plastics was observed during the 1970s, mostly due to the energy crisis of 1973, the environmental concerns and the consequent increase in oil prices (Katz, 1988; Manzini, 1993). Still, this was not the end of plastics production. According to P. Sparke, 'By 1970, many more new materials and manufacturing techniques had transformed the face of the everyday world' (Sparke, 2013: 131). 'They spoke a language of modernist utopianism to an audience that still trusted the power of technology to provide it with a better world, to improve the quality of everyday life, and to empower them as consumers' (Sparke, 2013: 131). To summarise the PUR trade names found during this research, Table 1.3 has been designed.

Table 1.3 Commercial trade names of PUR products available between the 1940s–1970s

PUR form	Trade name	Company	Reference
Rubber	I-rubber or I-Gummi	Bayer	(Meckel *et al*., 1996: 16; Prisacariu, 2011: 1)
	Vulkollan	Bayer	(Bayer *et al*., 1950 as cited in Hill *et al*., 1956: 927)
	Vulcaprene	ICI	(Harper *et al*., 1948 as cited in Hill *et al.,* 1956: 927)
	Adiprene	DuPont	(Hill *et al.,* 1956)
	Chemigum SL	Goodyear Tire & Rubber Co.	(Seeger *et al.*, 1953 as cited in Hill *et al.,* 1956: 927)
Fibres	Perlon U	Bayer	(Szycher, 1988: 298; Szycher, 2013: 1)
	Igamid U	Bayer	(Szycher, 1988: 298; Szycher, 2013: 1)
	Spanzelle	Courtaulds	(Lushington, 1967: 75)
	Fiber K	DuPont	(Carraher, 2013: 287)
	Lycra	DuPont	(Lushington, 1967: 131)
	Elura	Chemstrand	(Lushington, 1967: 131)
Coating or leatherlike product	Estane	B.F. Goodrich	(Meckel *et al*., 1996: 16; Prisacariu, 2011: 2)
	Desmopan	Bayer	(Meckel *et al*., 1996: 16; Prisacariu, 2011: 2; Verg, 1988: 394; Schneider, 2013: 56)
	Texin	Mobay	(Meckel *et al*., 1996: 16; Prisacariu, 2011: 2)
	Pellethane	Upjohn	(Meckel *et al*., 1996: 16; Prisacariu, 2011: 2)
	Elastollan	Elastogran	(Meckel *et al*., 1996: 16; Prisacariu, 2011: 2)
	Corfam	DuPont	(Lushington, 1967: 134; Fenichell, 1997: 281)
Foams	Troporit M	Bayer	(Szycher, 1988: 298)
	Bayflex	Bayer	(Schneider, 2013: 56)
	Baydur	Bayer	(Schneider, 2013: 57)
	Moltopren	Bayer	(Bayer, 1971: 138)

As observed in Table 1.3, PUR was being used to create many different types of materials (rubbers, fibres, films and foams), and dozens of commercial products were being sold under the production of this synthetic polymer.

CHAPTER 2

CONTRIBUTIONS TO A BIOGRAPHY OF POLYURETHANE — FROM THE INDUSTRY TO THE DAILY LIFE OF THE CONSUMER

2.1. Preamble

When researching the background to the historical framework of plastics, a general lack of knowledge concerning this subject has been observed. However, authors such as Mossmann (1997), Suggitt (1997), Waentig (2008) and Callapez (2000) have also reported this outcome in their publications.

> 'It is no coincidence that the history of plastics and the objects formed from them has to this day hardly been explored. On the one hand, it is a history of appliances which have not been thought worthy of attention by historians — whether of art, or of the economy or of industry. On the other hand it is a difficult history to write, requiring of art-historians a knowledge of chemistry, and of chemists a basic knowledge of the history of design' (Weinberg-Staber, 1984: 30 as cited in Waentig, 2008b: 13).

Although the previous citation dates back to 1984 and the history of plastics has evolved in the last decades, the relationship between the plastics, the industry and the consumer is under-explored and the reasons given above could be considered as up to date. Now, and concerning the subject intended in this chapter (polyurethane biography), the specific literature about plastics is not entirely focused on the particular work and experience of industrialists and designers with this material, or on the promoting initiatives of manufacturing companies in order to conquer consumer trust. Instead, the literature has generally focused on the chronological history of plastics development, on the time-frame period of their major entry in the world of art, fashion and design (1950–1960s) and on iconic plastic furniture objects and fashion items (Mossmann, 1997; Fenichell, 1997; Lushington, 1967; Sylvia, 1988, Sparke, 1993). According to F. Waentig, 'the history of plastics cannot be understood without the history of the chemical industry' (Waentig, 2008b: 20). Consequently, the study of iconic design and fashion objects from the 1960s and 1970s using polyurethane should also reflect that liaison. Within social, economic and political contexts, these objects are also the 'product' of a specific material and technological age. Therefore, the study of these objects should include this whole set of disciplines.

Even though general overviews on the history of polyurethane do occur in the literature (see Chapter 1, section 1.1.1), few studies focus on the relationships established between the industry and the designers, and between the polyurethane and the consumer (Mossman, 1997; Suggitt, 1997; Waentig, 2008b). Moreover, the collection of testimonies from industrialists and designers focusing their work on polyurethane has also been a poorly studied area and few studies concerning the national history of the plastics industry were found. The accessed literature about this subject is scarce and dispersed; studies entirely focused on the history of the polyurethane industry in Portugal are still missing.

The main goal of this chapter is to fill this gap. Secondly, it will be an initial attempt to gather and produce new documentation about the historical use of polyurethane (PUR foams and TPU fibres, films

and coatings) in fashion and design during the 1960s and 1970s. The research presented aims at building a bridge between the history and the technology, the industry and the object and between the product and the consumer. It intends to document the relationships established between polyurethane manufacture and processing industries and the reasons that led designers to select PUR over other materials.

By taking as case studies some PUR historical objects from the MUDE collection, the 1960s and 1970s are the period selected for this study. As previously mentioned (see section 1.4), these decades were typified by a revolution in the use of plastics in everyday life and in art (Katz, 1988; Jackson, 1998; Albus *et al.,* 1997; Sparke, 2013). Due to plastics' attractive qualities, many industrialists, designers and artists have considered these materials as a revolution in the production of their own creations. Along with granite and wood, plastics like polyethylene, polyester, polypropylene, poly(vinyl chloride) and polyurethane, among others, started to appear in galleries and art fairs (Albus *et al.,* 1997). PUR, as one of the most appreciated novelties of this time, gave the possibility to materialise a new lifestyle and enabled the rejection of conventional methods of manufacture that were offered by wood, stone, metal or glass (Katz, 1988; Fenichell, 1997; Jackson, 1998). Consequently, the manufacture and design production of PUR showed a drastic growth during these decades.

Since the MUDE collection includes PUR-based designs produced by renowned Italian, Danish, French and Portuguese designers (among others), this chapter is able to explore different contexts of polyurethane design history. Based on this diverse set of material testimonies, new records and evidences of polyurethane material and immaterial values were produced, and a historical perspective was built, contributing to the biography of this polymer.

In sum, this chapter focuses on the industrial pros and cons of PUR production in both manufacturing and design processes, on the documentation of marketing initiatives by Bayer and its work with international renowned designers, as well as on the documentation of Gufram's and Poltronova's singular work with PUR foams. Finally, it documents for the first time the foundation of PUR processing industries in Portugal and the work of Portuguese designers with this material.

This study followed inter- and multidisciplinary approaches. Both primary and secondary sources have been accessed, including monographs, dissertations, scientific journals, magazines, industrial periodicals and patents, factory catalogues, company flyers and brochures, videos and photographs, as well as personal testimonies from current and former industrialists and designers throughout the planning of written interviews. In this way, polyurethane foams, leathers and fibres were documented throughout from material and technical perspectives but most of all, through the historical and personal views of industrialists and designers.

2.2. Documenting the international relevance of polyurethane in fashion and product design in the 1960s and 1970s – an industrial point of view

For this section, manufacturing and processing (from chemical industries and design companies) patents dated between 1960–1981 and related to the use of PUR were selected, mainly because of the information enclosed in these documents. Patent documents are generally divided into five sections: abstract of the disclosure, background of the invention, summary of the invention, detailed descriptions (of drawings and claims), and references. Based on this structure, the identification of previous drawbacks, purposes of the inventions and material options considered for each case are clearly stated, as well as the technical and manufacturing requirements. These sections consist of valuable information for the subject covered here. Although other publications were sought (such as books and scientific articles), none showed the same level of detail and/or the indirect testimony of industrialists and designers as these official documents.

From a broader set of patents[23], fifty-four were selected to summarise the most common PUR applications and to cover the wide-range of polyurethane form possibilities. Based on this approach, this section discusses the novelty of this material in areas such as furniture design and ready-to-wear fashion from an industrial point of view. Within the studied set, fifteen patents are related to the production of chairs and seats from PUR foams (1963–1978), another fifteen are focused on TPU fibres (known as spandex) and their use in sports brassieres, foundation garments, swimsuits and compressive stockings (1960–1981), and the last twenty-four on polyurethane leatherlike products used in clothes and shoes (1966–1980). Therefore, PUR flexible and rigid foams, TPU fibres and elastic fabrics, and TPU films and coatings have been studied, based on the documentation of daily life objects. Also, the identification of companies working on PUR manufacture and design production, former commercial trade names and references to scientific publications was possible.

This section starts by focusing on the use of PUR in furniture design, chairs and seats and follows with a general overview about the potentialities of polyurethane elastic fabrics, foams, rubbers, leathers and coatings as materials to produce clothes, shoes and accessories.

[23] The whole set of patents can be accessed online on the platforms Google Patent Search and Espacenet (Patent search of the European Patent Office) as scanned documents.

2.2.1 Polyurethane in furniture design

It is known that PU is also a material for beautiful furniture.
That design history was written with it – considerable

Peter Ghyczy for *PUR, Costumer Magazine*, 2010 (Ghyczy, 2010: 12)

From the above statement by Peter Ghyczy, the key role of PUR in the revolution of furniture design is undeniable. Nevertheless, one question can still be posed. How has PUR actually changed this field?
For the production of furniture, polyurethanes were acknowledged (as expected) to be frequently used as expanded cellular materials, especially, as moulded, flexible and rigid foams[24]. In general, light weight, good abuse resistance and strength, resilient yieldable, simple and economic manufacture (e.g. single moulding operations) and the possibility of mass production were the most mentioned advantages for this preference (Hood, 1965; Lawson, 1965; Brosk, 1969; Cashen & Hermelin, 1969). Also, the authors stated the opportunity to explore novel and unusual designs, especially when the enhancement of the aesthetic quality of seats was intended (Brosk, 1969; Cashen & Hermelin, 1969; Dean, 1970; Taylor, 1972). According to Jeffrey Owen Brosk, in the past, conventional chairs and seats were commonly produced with wood and metal heavy frames or based on rigid and stiff plastics, which required various elements, supports and stiffeners (Brosk, 1969). With that, the aesthetic quality of furniture was limited to traditional lines and translated into legs, seat, back and arms. During the 1960s, some designers started to deviate from the use of these conventional lines; and Brosk's seat can be named as an example of that will (Brosk, 1969). According to his invention, 'a novel chair incorporating new and unobvious uses and applications of plastic properties' was proposed, and for this invention, polyurethane was mentioned as one of the preferred choices (Brosk, 1969: n.p.). As shown in Fig. 2.1A, this chair was comparable to a solid block that could be used by both adults and children. The inventor described that 'the outer shell is made completely of foam plastic which is somewhat flexible, yet has sufficient rigidity to support a person, (...) and the seating part is made completely of foam plastic which is sufficiently pliable, (...) resiliently yieldable and springy to return to its normal state when the person arises from the chair' (Brosk, 1969: n.p.). Further examples showing the creative use of PUR foams in chairs and the like are illustrated in the US Patents 3,476,497 and 3,495,874 (Figs. 2.1B and 2.1C) (Cashen & Hermelin, 1969; Dean, 1970). From these three patents,

[24] See for example, Ward (1963), Hood (1965), Lawson (1965), Brosk (1969), Cashen & Hermelin (1969), Dean (1970), Bartel (1970), Taylor (1972), Semplonius & Kolk (1972), Ghyczy (1972), Button (1973), Weidt (1974), Harris *et al*. (1974), Ambasz (1976), and Schoblom (1978).

the superstructure commonly found in conventional furniture has been eliminated and comfortable and 'unfurniture' items were produced (Cashen & Hermelin, 1969: n.p.).

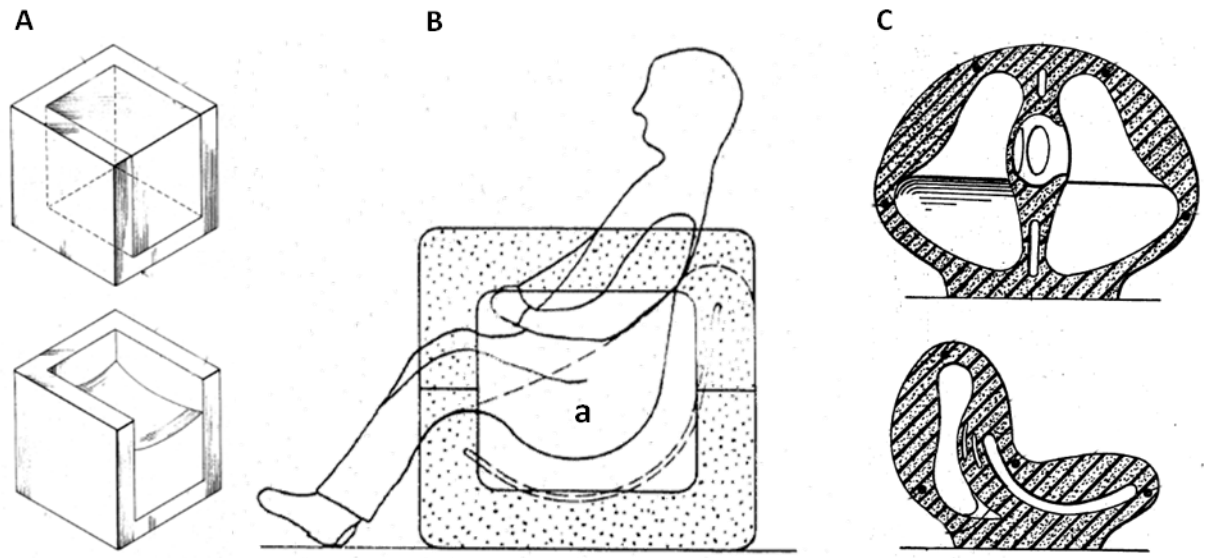


Figure 2.1 Examples of three foam chair designs illustrating unoccupied and occupied positions: (A) cube chair at rest (above) and in use position (bottom); (B) cube chair where the core (a) is a void and the dotted area illustrates the occupied position and (C) *Sea Urchin* chair at rest (above) and in use position (bottom) (adapted from Brosk, 1969: n.p.; Cashen & Hermelin, 1969: n.p.; Dean, 1970: n.p.).

Traditional uses of PUR foams in chairs and seats have also been found. For instance, Gunter Friedrich Bartel (Elastomer A.G., Switzerland) discussed the typical use of polyurethane moulded foams as cushioning (Bartel, 1970). However, the novelty reported by the inventor resided in the use of profitable processing processes brought by PUR. Bartel discussed the successive mould production of a foamed seat based on a rigid PUR foam frame, a semi-rigid PUR foam upholstery, and a layer of PUR flexible foam, without any part being removed from the mould during the whole process (Bartel, 1970). Since PUR foam formulations can be tailor-made into desirable compression ranges, this property was often mentioned to be used when better comfort and appropriate support for the user's body were intended. In the chair patented by William Paul Taylor, high compression ranges were selected for the PUR foam base (in the order of 35 pounds) while lower values were adopted for the intermediate foam layer (in the order of 26 pounds) (Taylor, 1972). In the US patent 3,669,499, the same principle was applied, 'the lumbar region of a person's back was supported by a heavier density cushion while the shoulder regions, which require less support, were supported by a softer foam cushion' (Semplonius & Kolk, 1972: n.p.).

Besides the expected presence of PUR in foamed chairs as cushioning and/or structural materials (as the examples previously shown), other possibilities have been acknowledged in this study. An

interesting case reflecting an uncommon use of PUR was the rigid seat shell designed by Ronald Button, where PUR foam was applied inside a rigid shell (Button, 1973). According to the inventor, this technical aspect was intended to reinforce the shell and to make it more comfortable to the user's body when seated (Button, 1973).

Further examples consist of the furniture modules designed by Karl-Adolf Weidt for Fritz Schaffer GmbH with PUR structural foams (Fig. 2.2) (Weidt, 1974). For this purpose, the author mentioned the possible use of *Polyurethane-Duromer* (Bayer). Weidt described that a surface resembling wood (grain-like structure) could be obtained by using this product, which proves the versatility of PUR products and their possibility to resemble natural materials (Weidt, 1974).

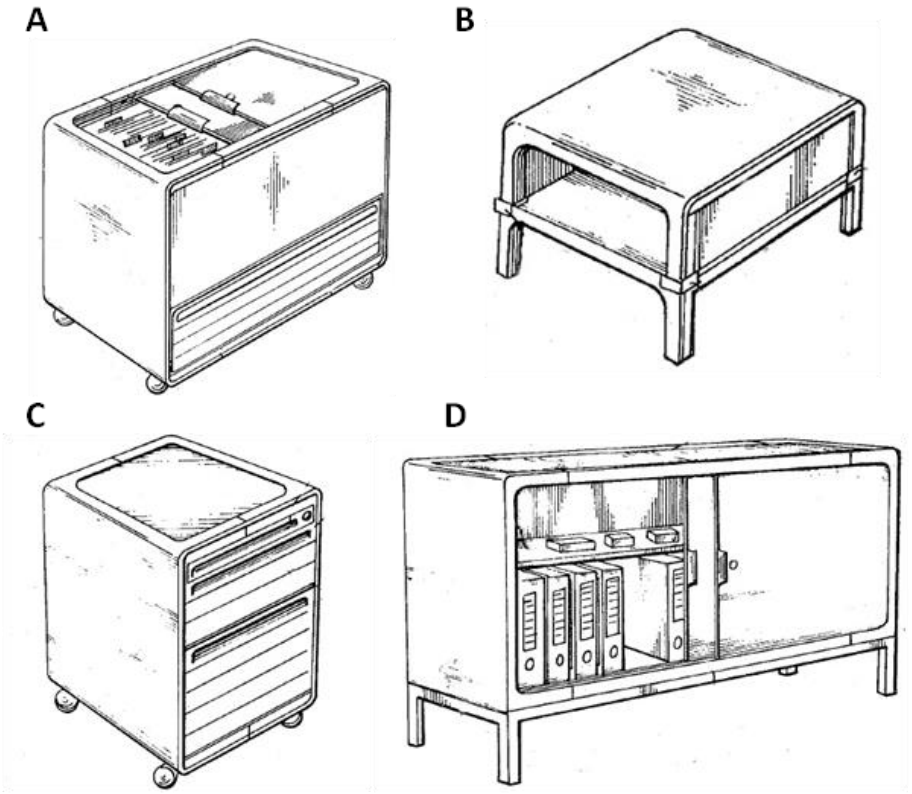


Figure 2.2 Examples of plastic furniture modules for offices: furniture formed as (A) card index chest with an upper sliding door; (B) table; (C) drawer cabinet; and (D) companion cupboard (adapted from Weidt, 1974: n.p.).

According to William White from Mobay Chemical Co., the product *Polyurethane-Duromer* (known as a structural foam) 'is the name of a new material which can produce a strong structural sandwich composite molding with integral solid urethane skins and a microporous core' (White, 1969: 1). Therefore, this material could be used to produce lightweight (effortlessly movable objects) and highly rigid (strong resistance) furniture items (Weidt, 1974).

Apart from the useful advantages of polyurethane, some drawbacks were also reported in the selected patents. PUR rigid foams were described as 'friable materials useful mainly for filling voids' (Hood, 1965: n.p.; Harris *et al*., 1974), and flexible foams as low tear resistance materials (Hood, 1965: n.p.). However, some solutions for these problems have been also reported by the inventors. According to Bruce G. Hood, PUR flexible foams are tougher than rigid foams and can be used to distribute localized pressures (Hood, 1965). To overcome the flaw of PUR flexible foams, some inventors commonly suggested the use of superficial skins (Ward, 1963; Hood, 1965). According to I. E. Ward, these skins are tough, elastic and resilient and their thickness can be controlled by the use of pre-heating moulds or external heat (Fig. 2.3) (Ward, 1963).

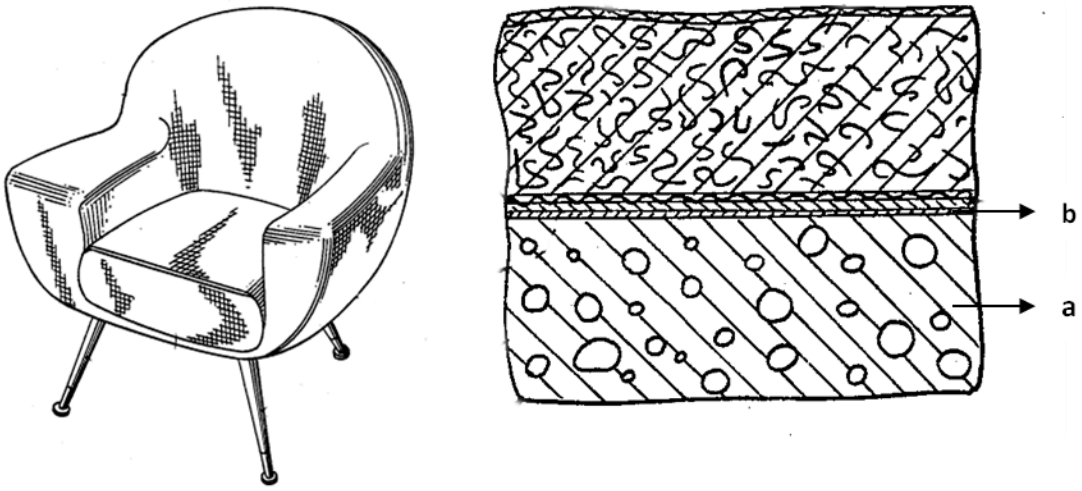


Figure 2.3 Patented upholstered seat article. Left: perspective view of the seat. Right: sectional view of the seat polyurethane foam (a) and skin (b), underneath the fibrous pad (adapted from Ward, 1963: n.p.).

Among the fifteen patents related to the production of PUR-based furniture, one chair was related to a case study from the MUDE collection, i.e., the cellular plastic chair designed by the Hungarian émigré Peter Ghyczy[25] (Fig. 2.4), currently known as the *Egg* chair (Appendix III). From the study of this patent, it is interestingly acknowledged that PUR was mentioned as the preferred material (Ghyczy, 1972). According to Ghyczy, 'although any cellular plastic could be used' (...) 'it is preferred to mold the chair body and back from a rigid polyurethane foam' (Ghyczy, 1972: n.p.). Moreover, he stated the preferable use of a 'molded rigid polyurethane foam having an integral skin' (Ghyczy, 1972: n.p.); from this, Ghyczy produced an economical and comfortable chair, which could be easily moved and adaptable to many uses (indoor and outdoor) (Ghyczy, 1972).

[25] Peter Ghyczy (1940-) left his native Hungary in 1956 because of the Hungarian revolution for West Germany (garden(egg)chair, n.d.). In his words, 'My designs (…) are based on technical solutions that I apply in a new way. Again and again, technology plays the central role in determining their form—that is, it's the force of reason that pervades the design' (Ghyczy Design Selection BV, 2015).

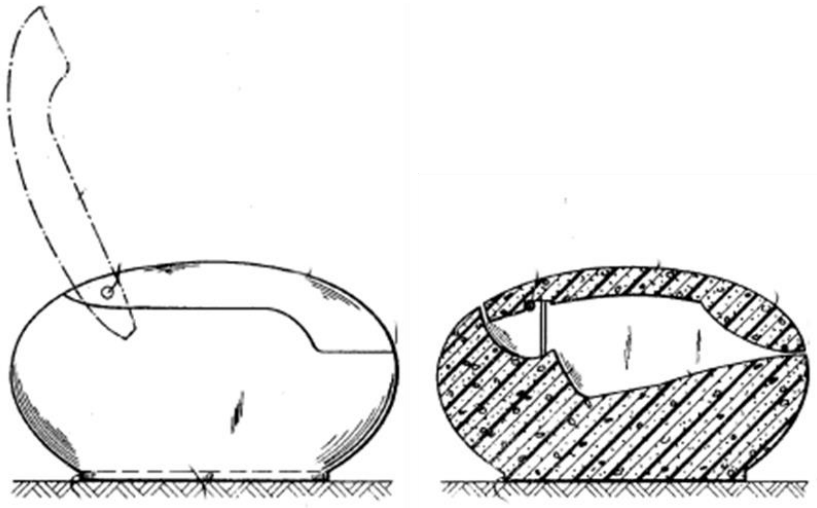


Figure 2.4 Cellular plastic chair patented by Peter Ghyczy. Left: View of the ellipsoidal-shaped chair when open (dash dot line) and closed (solid line). Right: sectional view of the patented chair when closed showing the rigid polyurethane foam body (adapted from Ghyczy, 1972: n.p.).

In a recent interview, Ghyczy talked about the production of this chair to *PUR Customer Magazine*, and from this document, more information has been added about his material choice (Ghyczy, 2010). Ghyczy was invited to work in Lemförd by Gottfried Reuter (founder of the company Elastogran) to start a design centre. From this invitation, the *Egg* chair was developed. According to him, 'it was an exciting, nearly anarchist time (...), we designed all kinds of furniture out of polyurethane: chairs, tables, shelves and complete kitchens' (Ghyczy, 2010: 13). Moreover, 'polyurethane was in this area supposed to replace the material wood' and 'Dr Reuter allowed us total creative freedom and at the same time let us use the design centre to welcome customers and to demonstrate what is possible with polyurethane in future' (Ghyczy, 2010: 13). From this testimony, the novelty and the material experimentalism brought by polyurethane are clearly stated. The freedom of design and the potentialities of new shapes and lines are definitely the motors of polyurethane use in design.
On the other hand, alternatives to polyurethane were also mentioned in the accessed patents and the main suggestions to replace these foams were PVC, polyethylene, polypropylene, polyether, polyester, polystyrene, poly(acrylonitrile-butadiene-styrene), rubber and the like (Ward, 1963; Lawson, 1965; Brosk, 1969; Weidt, 1974; Schoblom, 1978).

2.2.2 Polyurethane in fashion

Polyurethane elastic fibres were also patented for their role in the production of fabrics and ready-to-wear fashion garments and accessories. For this part of the research, the gathering of patents including drawings and reporting specific advantages related to the use of these fibres in clothes has been more

difficult. Compared to the previous case (foams in furniture), fewer patents have been found and most of the available documents were assigned to manufacturing industries. This fact could mean that fashion design companies were not so active in patenting their creations, or that a smaller number of these patents are available (online). Nevertheless, interesting cases have been found and the use of polyurethane fibres (often stated as spandex) in ready-to-wear fashion garments and accessories is discussed.

Within the selected set of fifteen patents, eight are associated with the manufacture of elastic fibres and fabrics, and seven with the design of fitting garments and wearable accessories. From the first eight, three are assigned to the E. l. DuPont de Nemours and Company (USA) and two to the Farbenfabriken Bayer Aktiengesellschaft (Germany), which once more confirms these two companies as the most important manufacturers of PUR polymers, in the 1960s and 1970s.

A common aspect reported in six of the selected manufacturing patents was the need to replace rubber as an elastic thread (Koller, 1960; Yuk, 1962; Schilit, 1963; Oertel *et al*., 1969; Rosendahl *et al*., 1969; Morancy, 1971). The most mentioned reasons were its poor abrasion resistance, low elastic moduli, poor stability to UV light and high cost of production. Furthermore, rubber yarns were reported to be produced by cutting rubber sheets into tiny strips that were difficult to knit into a fabric (Schilit, 1963; Morancy, 1971). Consequently, several industrials reported that it was an almost impossible task to obtain fine denier yarns from rubber (Koller, 1960; Schilit, 1963). From this context, the development of replacements was definitely a goal of the textile industry and for that, PUR was often mentioned as a good option (Koller, 1960; Schilit, 1963; Oertel *et al*., 1969; Rosendahl *et al*., 1969; Morancy, 1971).

One of the first goals of chemists was to improve the wearing comfort and the dye ability of rubber threads (Koller, 1960). To this end, Charles Richard Koller (DuPont) proposed, in 1960, the manufacture of filaments from 'linear polymers comprising amides linked to polyethers through urethane groups' (Koller, 1960: n.p.). As asserted by the inventor, 'yarns of this invention have many advantages over rubber threads'; namely, 'they may be spun readily into multifilament yarns and (...) low denier filaments, (...) have a very low inherent color, superior abrasion resistance, may be dyed by common dyestuffs, need no plasticizers, (...) have a good resistance to perspiration or greases, (...) and are capable of very quick elastic recovery' (Koller, 1960: n.p.). Roberta J. Schilit (DuPont), in the US Patent entitled 'Elastic filaments from polyester urethane-urea polymers', had the same goal (Schilit, 1963: n.p.). Her[26] invention resulted in a polyurethane fibre with 'less failure by breaking' and 'greater

[26] Curiously, although Roberta J. Schilit is from DuPont, she refers to Vulcollan® (trademark from Bayer) as a recently developed and well-known elastic fibre (Schilit, 1963). However, her reference aims to draw attention to the unawareness of companies to the usefulness that resides in the 'critical selection of starting materials necessary to make a suitable elastic fiber' (Schilit, 1963: n.p.). This lack of knowledge was clearly stated in the words, 'nowhere is it recognized or taught which diisocyanates, which polyesters, and which diamines together yield elastic fibers having the necessary properties for commercial textile use' (Schilit, 1963: n.p.). This proves the limited knowledge about the formation of polyurethane network (supramolecular structure) and crosslinking points in the beginning of the 1960s, as well as the unknown possibility to tailor-

ultraviolet durability than rubber' (Schilit, 1963: n.p.). Harald Oertel (Bayer) also discussed the dye ability of elastic fibres as an advantageous quality of polyurethane fibres over rubber threads since common dispersion dyes could be used (Oertel *et al*., 1969). Chemists such as Rosendahl and co-workers (Bayer) and Morancy (Lawson Products, Inc.) were also supporters of polyurethane elastic fibres qualities (Rosendahl *et al*., 1969; Morancy, 1971).

On the other hand, some drawbacks have also been mentioned, especially during the manufacturing process (Yuk, 1962). In the US patent 3,039,895, the use of a lubricant was reported to be necessary to prevent the hardening of these fibres (by sticking) and the consequent erratic running tensions on fabrics (Yuk, 1962). Regarding the long-term stability of spandex, discolouration was mentioned as one of its weakness (Rausch & Sayigh, 1970).

Nevertheless, this short survey enabled the identification of polyurethane filaments as one of the main elastic fibres serving the textile industry of stretchable and fitting clothes during the 1960s and 1970s. This success was especially due to their superior quality over rubber yarns. In the words of William F. Morancy, 'spandex is far superior to natural rubber in terms of elasticity, shelf-life, dye-acceptance and stability to oil, dry-cleaning chemicals, sea-water, sunlight and ultra-violet' (Morancy, 1971: n.p.), making it suitable for the production of corsetry, underwear, bathing wear and stockings (Oertel *et al*., 1969). In the following paragraphs, the advantages of such uses are discussed with examples of compressive stockings, women's slips, sport gloves, athletic brassieres and swimsuits.

For the production of a pair of compressive stockings, a fabric incorporating yarns of nylon and TPU filaments has been chosen to provide superior two-way stretch, excellent dye ability and a great feel (Fig. 2.5) (Burleson & Holmes, 1963). According to the inventors, using polyurethane as an invisible yarn (woven in nylon) made possible to obtain stockings showing excellent fitting properties and compressive support without compromising the fine aesthetic finishing (Burleson & Holmes, 1963).

Besides stockings, women's clothes such as slips, undergarments and nightgowns were also using TPU fibres. In the US patent 3,339,553, the aim was to produce a light weight and comfortable garment, showing closer contour fit and full freedom of movement (Ritter, 1967). For that, spandex was mentioned as the preferred material due to its nature to mould itself to the form of the wearer's body (Ritter, 1967). According to Ritter, 'this fiber has high breaking elongation, excellent breaking strength, excellent holding power, good tensile recovery, excellent durability, excellent flex resistance, very good uniformity, good resistance to abrasion and good resistance to chemicals and cosmetic agents' (Ritter, 1967: n.p.).

made PUR structure into desirable properties. This subject was a challenging research topic for the chemical industry in the following decades (see page 18).

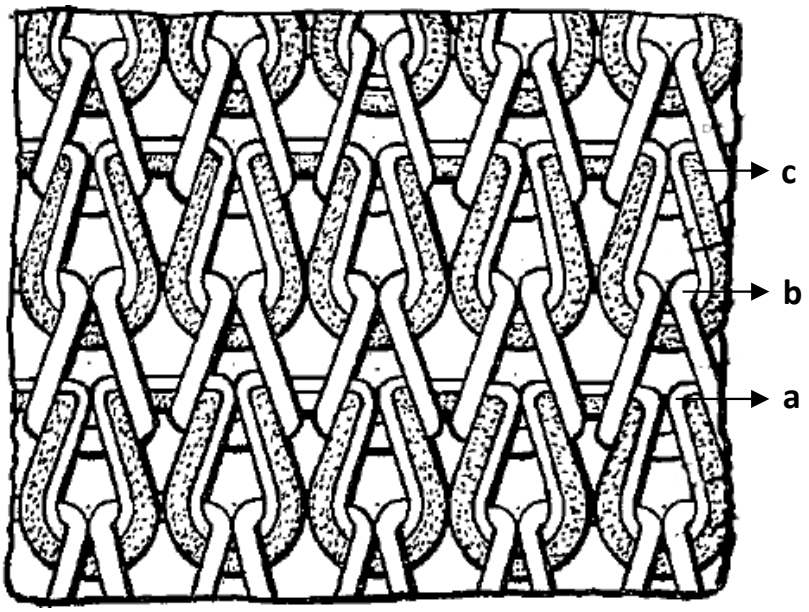


Figure 2.5 Enlarged and stretched diagrammatic view of the stocking fabric showing the presence of 20 denier nylon yarns (a), 40 denier nylon yarns (b) and 70 denier polyurethane yarns (c) (adapted from Burleson & Holmes, 1963: n.p.).

To produce a sport glove, the use of ‘spandex fabrics’ was suggested as a suitable replacement of natural or synthetic leatherlike products (prior art methods) (Stanton, 1971). As reasons, the author mentioned the difficulty to put on and remove the glove, the weak resistance to repeated wearing, the loss of fit and feel and the lack of moisture resistance generated by perspiration (Stanton, 1971).
For the production of a swimsuit, the preferred selection of a fabric consisting of 75% nylon and 25% TPU was mentioned (Dottinger, 1976). Mostly, because ‘swimsuits made out of this kind of material have the advantage that they adapt especially well to the individual body sizes’ and allow ‘only minimal air-penetration’ (Dottinger, 1976: n.p.).
The last two examples illustrate the use of TPU fibres to produce sports brassieres (Fig. 2.6). In order to stop the constant bouncing of breasts commonly disapproved by women runners, in one case (Fig. 2.6, on the left), the author selected a ‘cotton-spandex fabric or cotton-spandex-polyester’ (e.g. 42% cotton, 16% Lycra, and 42% polyester) because 'it is strong and non-irritating’ to the skin and ‘resists salt from perspiration’ (Schreiber, 1979: n.p.). In the other case (Fig. 2.6, on the right), the use of the stretchy fabric POWERKNIT® (trademark) was recommended. According to him, this fabric was a combination of 20% TPU and 80% nylon yarns and was selected due to its lightweight, soft and elastic properties and because it limited the movement of breasts without inadequate or uncomfortable pressures (Schreiber, 1979).

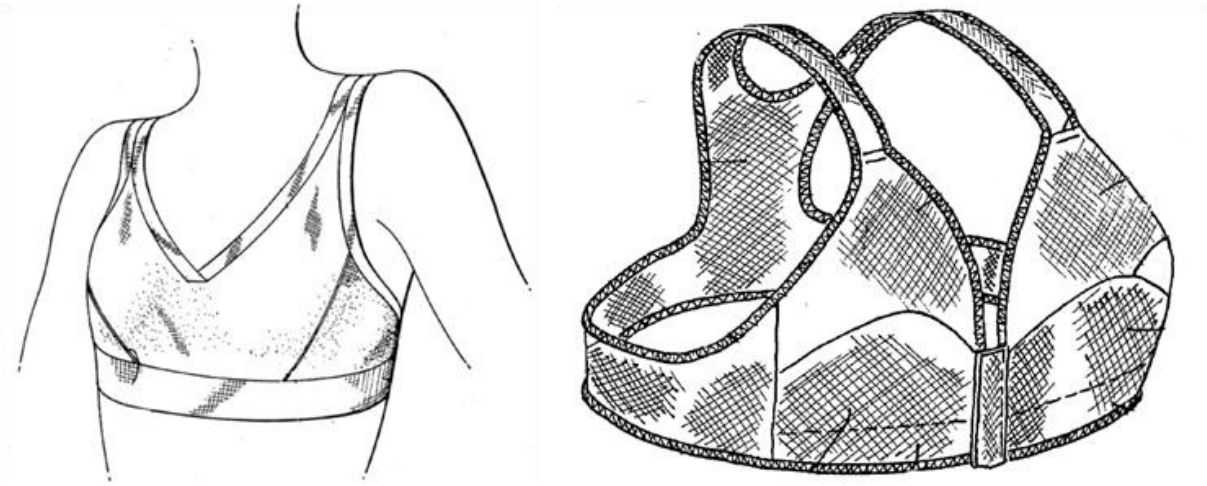


Figure 2.6 Examples of patented sports brassieres (adapted from Schreiber, 1979: n.p.; adapted from Dell & Clifford, 1981: n.p.).

From this approach, the common use of TPU elastic fibres in fitting garments and accessories is confirmed and their valuable use is documented through an industrial perspective. The common adoption of the term 'spandex' (as synonym of TPU elastic fibres) is recognised as a specific trademark of the Firestone Tire & Rubber Company (USA), and additional commercial trade names were revealed. For example, *Fiber K*® was assigned to DuPont and *Vyrene*® to the US Rubber Company (Burleson & Holmes, 1963; Gerald, 1967).

Finally, this section follows on to the documentation of the use of PUR leatherlike products and foams in ready-to-wear fashion garments and accessories. Concerning the use of artificial leathers based on TPU, the search for patents was a difficult challenge since a wide range of material possibilities was found to be included in this field. As examples of this variety, poromeric products (porous leather substitutes), microporous surfaces (with porous invisible to the human eye), suede-like sheet materials and leather finishing coatings (sole TPU or blended) were found. The use of PUR foams was frequently found in patents related to the design of shoes.

With the aim to discuss and summarise the pros and cons of these materials, the data set is composed of twenty-four patents (1966–1981). From this set, approximately half were entirely focused on specific fashion items such as clothes, accessories and shoes[27]. From a general overview, a higher number of patents were assigned to Japanese companies, which, as previously mentioned, correlates with the globalization of the PUR market to countries outside Europe and USA since the 1970s.

[27] See for example, Niconchuk (1966), Rosing *et al*. (1967), Johnson (1968), Kogert and Schwab (1971), Aldrich (1973), Hirsch (1974), Oka and Wakabayashi (1974), Cunningham and Bastle (1976), Frey and Schieber (1978), and Landay and Wolf (1981).

For the ready-to-wear fashion industry, PUR has been mostly used to produce leather clothing such as jackets, skirts, shoes and accessories (e.g. gloves, luggage cases and bags) (Matsushita *et al*., 1968; Kogert & Schwab, 1971; Morrissey & Hess, 1971). One of the mentioned reasons for this was the high quality of PUR leatherlike products and their use as replacement of former natural leather equivalents. As stated by Matsushita and co-authors, 'the demand for a synthetically produced material, which can be utilized in the same manner as natural leather is well known in the art', nevertheless, 'the prior art methods have failed to provide a synthetic leather meeting the requirements of a true leather substitute' (Matsushita *et al.*, 1968: n.p.). In agreement with this statement, Kaneko stated that 'known artificial and imitation leathers are for the most part deficient in cold resistance, heat resistance, air permeability, moisture regain and touch or texture' (Kaneko, 1970: n.p.). To overcome these flaws, several chemists and engineers adopted urethane-based thermoplastic elastomers. Matsushita *et al*. from the Toyo Rubber Industry patented a vapour permeable artificial leather (Fig. 2.7) with a surface layer of polyurethane-urea and multiple layers of fibrous nature (Matsushita *et al.*, 1968); and Okazaki and co-workers from Toray Industries produced a microporous artificial leather with three layers of TPU above a fibrous substrate with the goal to mimic the properties of a high-class natural leather, the German Box Calf (Okazaki *et al*., 1974: n.p.).

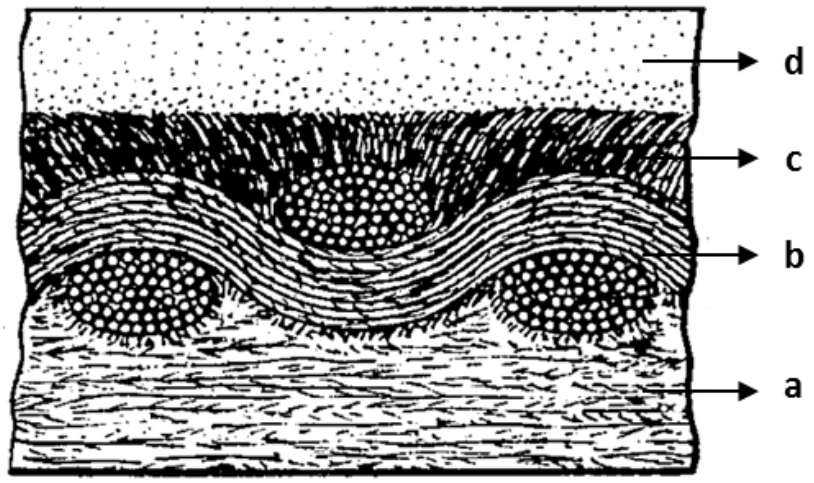


Figure 2.7 Cross sectional view of a patented vapour permeable synthetic leather showing a layer of random webs (a), a plain-woven cotton fabric; a napped cotton fabric (c), and a polyurethane coating (d) (adapted from Matsushita *et al*., 1968: n.p.).

Microporous leathers, as reported, consisted on a fibrous base of a woven or non-woven fabric, impregnated and coated, with a much thinner layer of a microporous polymer (Cunningham & Boutle, 1976). As described in the US patent 3,982,335, 'the non-woven impregnated (...) fibrous fabric layer is used to impart strength, (e.g. tear strength), flexibility and other leatherlike properties to the

material, while the thin overlying polyurethane layer gives resistance to surface abrasion and to ingress of liquid water' (Cunningham & Boutle, 1976: n.p.). From this, artificial products closer to natural leather could be obtained and characteristics such as 'natural appearance and feel', 'desirable drapeability and flexibility' (Matsushita *et al.*, 1968: n.p.), and formation of similar crazes when bended or flexed (Okazaki *et al*., 1974: n.p.) were mentioned as valuable qualities.

In addition to the single use of polyurethane in leatherlike products, blends of TPU with other synthetic materials have been acknowledged. One reported example has been the blend of nitrocellulose with TPU. According to a patent assigned to Rohm and Haas, nitrocellulose had been a common prior art method for finishing natural leather (Lewis & Yunaska, 1974). Nevertheless, disadvantages were observed (e.g. lack of sufficient flexibility) and so new options were developed (Lewis & Yunaska, 1974). For that, a nitrocellulose-modified urethane coating was proposed and better results concerning flexibility and wearing properties were obtained (Lewis & Yunaska, 1974). Similarly, Bayer was also patenting blends of TPU with nitrocellulose with the purpose to improve the flexibility of prior nitrocellulose films (Eimer *et al*., 1974).

Beside these possibilities (poromeric, microporous and finishing coatings), polyurethane was also referred for use in the production of suede-like sheet materials (Noda & Shimamura, 1971: n.p.). As stated by workers from the Kurashiki Rayon Company, 'it is preferred to use mainly polyurethane elastomer, which has suitable pliability and excellent strength' (Noda & Shimamura, 1971: n.p.). Therefore, TPU films and coatings proved their versatility in the design of specific surface textures for leatherlike products, such as glossy, porous and microporous suede.

Patents illustrating fashion items using PUR foams and leather products were more difficult to find; nevertheless, some cases have been found and are discussed in the following paragraphs.

By starting the discussion with shoes, these have been the most commonly found examples of fashion items using these materials[28]. In US patent 3,570,149, the aim was to produce a shoe particularly suitable for skiing, mountaineering and industrial use (Kogert & Schwab, 1971). For that, materials capable to meet strict requisites such as being watertight, resistance to cutting, light weight and capacity to retain shape were sought. For this, TPU coatings have been selected since only one, or at the most, two layers would be necessary. This enables the lightweight of the shoe to be kept as well as the water-tightness and shape-retention properties (Kogert & Schwab, 1971). Still in line with sport goods, a different patent showed the production of a ski boot exhibiting special ankle support based on the application of a layer of polyurethane foam (Johnson, 1968). The Brookfield Athletic Shoe Company patented other sport shoes where polyurethane foam was applied in the construction of the sole (Landay & Wolf, 1981). In this case, the sole was not entirely produced with PUR foams, but

[28] See for example, Johnson (1968), Kogert and Schwab (1971), Hodge and Patsis (1972), Cunningham and Boutle (1976), and Landay and Wolf (1981).

divided into an outsole (made of rubber) and a midsole (made of injection-moulded PUR foam) (Landay & Wolf, 1981). According to the inventors, the combination of rubber and PUR resulted in a 'lightweight and flexible shoe compressively conformable to the flexing foot and having strong and long wear' (Landay & Wolf, 1981: n.p.). All-rubber shoes have been reported to show a tendency to tire the user and to require expensive manufacture processes. Soles entirely made of PVC were mentioned to show poor grip and little resilient cushioning, and polyurethane soles, to provide poor grip and wear resistance. Therefore, the combination of PUR and rubber made it possible to produce a sole showing resilient traction (rubber function), flexibility, light weight as well as compressive effect (polyurethane function) (Landay & Wolf, 1981: n.p.). Nevertheless, the wide world of polyurethane shoes was not reduced to sport goods and US Patent 3,982,335 reflected another application (Cunningham & Boutle, 1976). In this patent, TPU-based uppers were selected for the design of formal men and women's shoes (Fig. 2.8) (Cunningham & Boutle, 1976). According to the inventors, the prior use of natural leather uppers required the need of a "break-in" period in order to obtain a comfortable fitting (Cunningham & Boutle, 1976). With the use of polyurethane leatherlike products, the stretchable property of this material allowed the upper to readily accommodate to the particular shape of the wearer's foot and eliminate undesirable pressure (Cunningham & Boutle, 1976). As a result, a water vapour permeable microporous sheet of elastomeric polyurethane material was produced and used for the construction of the shoe.

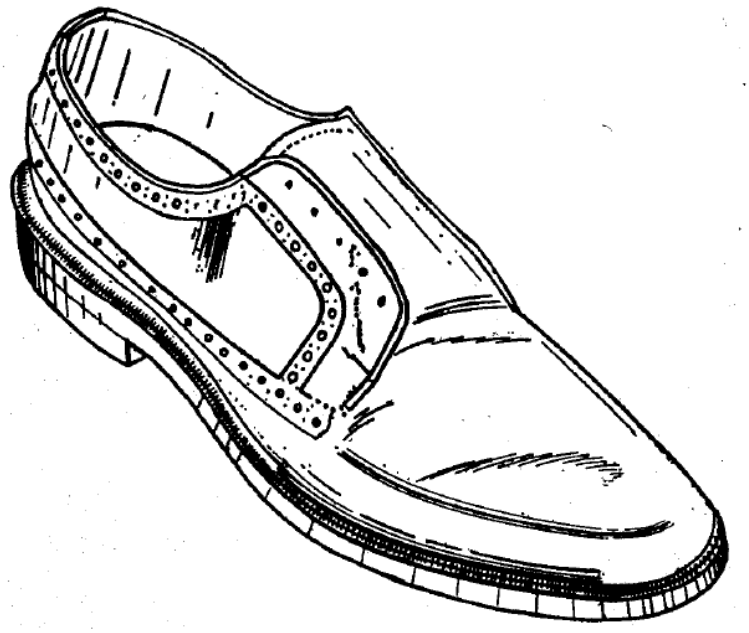


Figure 2.8 Perspective view of a patented shoe with a polyurethane microporous sheet as the shoe upper (Cunningham & Boutle, 1976: n.p.).

When leather goods required glossy finishes, polyurethane was also an option. One example was patented in 1972 by the E. I. DuPont de Nemours and Company (Hodge & Patsis, 1972: n.p.). In this case, the goal was to produce 'glossy vapor permeable finishes (...) free from surface tack' and possible for both natural and synthetic leathers (Hodge & Patsis, 1972: n.p.). Although prior art methods were offering coatings for these purposes, most of them were non-porous, failed on flexibility, scuff resistance (crack and loose shine), and presented surface tack (Hodge & Patsis, 1972). To fulfil this need, chemists from DuPont patented a coating based on blends of TPU, PVC and polysiloxane, resulting in a microporous layer showing water vapour permeability and glossy appearance (Hodge & Patsis, 1972). One patent showing the use of PUR moulded foam for a women's shoe heel was also included in this discussion. In US patent 3,258,861, Niconchuk made use of the strength, resiliency and density range offered by PUR rigid foams to produce footwear heels that, according to their shape and size, could be adapted for ladies', men's or children's shoes, without compromising comfort and providing light weight (Niconchuk, 1966). For the production of luggage cases, PUR foams were also found to be commonly applied because of the economical effect brought by the lightweight foam. As stated by workers from Samsonite, 'with the advent of air line travel, the weight of luggage has become quite important, since the transportation of an air passenger's luggage, in excess of a nominal weight, is very costly' (Rosing *et al*., 1967: n.p.). Therefore, the opportunity to replace former products, which consisted on wood or metal heavy frames, was particularly imperative for this company (Rosing *et al*., 1967).

Leatherlike products were also being widely explored. In Japan, Kigane and co-workers (from Teijin Limited) were producing durable, breathable and pleasing microporous leathers from polyurethane (Kigane *et al*., 1972). In Germany, Reischl and colleagues (from Farbenfabriken Bayer Aktiengesellschaft), described these materials as useful not only for the production of fashion items such as ladies' shoes, handbags, purses, belts and raincoats, but also valuable for upholstery purposes (Reischl *et al*., 1973: n.p.). An example of women's sportive bag using polyurethane resembling leather was illustrated in US patent 4,096,929 (Frey & Schieber, 1978).

Other items exploring PUR were found by curious means. Within the set of twenty-four documents, an interesting case is related to the production of wear-resistant garments (Aldrich, 1973). In this patent, the useful life of shirts and the like was described to be intrinsically connected to the limited wear life of components such as collars, neckbands and cuffs (Aldrich, 1973). As stated by W. E. Aldrich, these components were known to exhibit a tendency to ball, pill, be stained and discolour, mainly due to the short length of fibres and the tendency to absorb oil (Aldrich, 1973). Although prior art methods made use of polymer coatings to minimise these drawbacks, the desirable requirements were not successfully fulfilled. With the introduction of PUR, a novel composition was presented, exhibiting 'the

ability to repel the absorption of oil and to release soil when combined with synthetic and cellulosic fabrics or blends thereof' (Aldrich, 1973: n.p.).
Like previous cases, in this set of patents, additional information was collected. For example, *Estane®*, *Texin®* and *Elastollan® TN 61 EH 98 AK* were reported as trade names of possible TPU coatings.

In general, the unlimited properties of PUR as well as the versatile forms and uses offered by this polymer have been explored through the discussion of industrial patents assigned to both manufacturing and processing industries of furniture and ready-to-wear fashion garments and accessories. From this, there is no doubt that PUR brought novel design possibilities, new shapes and better comfort as well as simple manufacturing processes that enabled designers to conduct experiments with the material and push their creativity to the limit.
Moreover, the fundamental role of Bayer in the development of polyurethane chemical research is undeniable. Therefore, the role of this company in the transfer of this knowledge to designers is discussed in the following section.

2.3. The role of Bayer in consumer acceptance of polyurethane – Bayer and the *Visiona* exhibitions

As previously mentioned, Bayer's role in the breakthrough of PUR chemistry and the PUR wide polymer class has already been focused on in several studies (see Chapter 1, section 1.1.1). In summary, polyurethane was discovered by Otto Bayer in 1937, and, although this first discovery was by chance, polyurethane was manufactured into customized materials about ten years later, offering a wide range of material forms and application purposes, until today. Nevertheless, to our knowledge, the acceptance of this polymer by the public has not been commonly explored in the literature; similarly, Bayer's partnerships with international renowned designers and the company's role in polyurethane promotion needs to be considered in depth[29]. Therefore, this section is an initial attempt to gather new documentation on the subject, through the access of both primary and secondary sources.
Before starting to introduce this subject, it is important to highlight the research work already conducted by Friederike Waentig into the German context, which tends to contradict the common tendency of plastics historical research (Waentig, 2008b). In her PhD thesis, entitled 'Plastics in Art, A

[29] Although the work of Bayer has not been commonly explored, one found exception was the published literature about the American company DuPont by S. Fenichell (Fenichell, 1997: 228), J. L. Meikel (Meikel, 1995), D. Rhees (Rhees, 2004 as cited in Ball, 2004: 757), N. J. Moreau (Moreau, 2005) and P. Sparke (Sparke, 2013). These publications focus on the company's work on promoting initiatives of its materials in advertisements, industrial fairs and shows.

Study from the Conservation Point of View', not only material and conservation issues were explored but also the historical and cultural contexts of the plastics industry in Germany (Waentig, 2008b). F. Waentig not only focused on the relationships established between industry, plastics and design, but also on their impact into the daily life of the German consumer. For that, Waentig selected popular-science publications, scientific monographs, congress reports, journals, plastics magazines and advertisements, covering a wide set of documents that could contribute to the biography of a complex material. Still in line with this, Waentig says that 'the literature-based research into the history of plastics was both very complex and wide-ranging' (Waentig, 2008b: 15–16). This multiplicity of references was also observed in the current study, proving once more the difficulty involved in the study of areas that include industry, chemistry, history, art, design and ultimately, conservation. Nevertheless, from this and Waentig's other publications, some important remarks have been taken, in particular, with respect to the German industry during the 1960s and 1970s; and Bayer's role in the promotion of its 'chemical materials' (Waentig, 2002; 2008b; 2012). Since the information enclosed in the aforementioned references was still insufficient for what concerns the biography of PUR design history, primary sources have been added to this study, which will be described later. Still, one study entirely focused on the work of the designer Verner Panton was included as literature-based research (Vegesack & Remmele, 2000). As previously mentioned (see Chapter 1, section 1.1.1), Verner Panton is an essential reference of designers experimenting with new materials in the 1960s and 1970s and one of Bayer's hires for the promotion of its materials. Furthermore, PUR was part of his experiments and probably, one of his preferred materials in these decades. Similarly, specialist literature about Joe Colombo (Fagone & Favata, 2011) and Olivier Mourgue was sought. However, publications focused on Olivier Mourgue's work were difficult to find and primary sources such as interviews and other records were included (Mourgue as cited in An lnterview, 1968). These two designers were also part of Bayer's *Visiona* family and are known as singular leading figures of design in this period, to which PUR offered a wide range of possibilities. Another reason for the start of this deeper research into the work of Bayer with these designers resides in the presence of PUR-based iconic objects by Panton, Colombo and Mourgue in the MUDE collection. Documenting their partnership with companies manufacturing this polymer stood out as a crucial goal. In the MUDE collection, the work of these designers can be seen in the *Panton* chair (1968) and the *Living Tower* seating system (1968–1969) by Verner Panton; in the *Elda 1005* armchair (1965), the *Addictional Living System* lounge chair (1967–1968) and the *Tube* chair (1969–1970) by Joe Colombo; and in the *Djinn* series of sofas (1965) by Olivier Mourgue.

In this way, the research into the work of these designers with Bayer has started and new and relevant documentation has been found, proving the novelty of this section[30]. For that, this research included access to and the assessment of primary sources, in particular, documents from the Bayer Corporate Archive about *Visiona* exhibitions. From this archive, precious records have been studied including videos, photographs, correspondence letters and brochures and fliers (press releases from Bayer in-house newspaper) dated from 1968–1974. In addition, photographs from the Verner Panton Design Archive (Basel), articles from the German journal *Der Spiegel* (section 'Kultur', 1970–1972) (Wohnen, 1970: 149; Wohnen, 1972: 98–101), Bayer's biography books (Verg, 1988; Schneider, 2013), and advertisements in the *New Scientist* journal (1971) have been selected, given the information enclosed in these documents.

This section starts from a brief summary of the German context of this period and on Bayer's industrial framework; and follows on to the documentation of *Visiona* exhibitions through the study of historical design objects made with PUR.

Since the history of the plastics industry in Germany was well studied and reviewed by F. Waentig, a brief summary only is presented here. This summary focuses on the country major historical marks during the 1960s and the accomplishments of Bayer with PUR for the production of fashion and design items.

In the 1950s, Bayer was witnessing the prosperous growth of the West Germany plastics industry, especially, after the foundation of the Federal Republic in 1949 (Waentig, 2008b: 44). As mentioned by Waentig, before this important historical mark, the German public generally showed a 'plastophobic' temperament (Waentig, 2008b: 46). Moreover, the production of plastics was limited to a certain amount and its main goal was the replacement of other materials (Waentig, 2008b). As previously mentioned (see Chapter I), along with the technological development imposed by the Second World War, the economic growth in the USA and the implementation of the Marshall Plan was observed and the chemical and industrial knowledge was only gradually transferred to civilian everyday life. Along with these economic initiatives, actions for the promotion of plastics and the concept of 'good design' started to be held during the 1950s, and Germany was no exception (Waentig, 2008b). In 1953 a German council, called the *Rat für Formgebung*, was founded exclusively dedicated to design, and in the following years, several exhibitions took place in the country. Namely, the first 'Plastics Exhibition' in Darmstadt; the *Die gute Industrieform* in Munich (first industrial design exhibition); the *Die gute Form* (good design) between 1955–1975 (twice a year); the *Kunststoff für Alle* (Plastics for all) in 1956; and the *Kunststoffe – gut geformt* in 1960, in Frankfurt am Main (Waentig,

[30] Although other plastics (such as polyamide fibres, typically known as nylon, PVC and polyester) and companies (for example, DuPont and ICI and Dunlop) have also played a major role in the public acceptance of these new materials, this part of the research is exclusively focused on PUR and Bayer.

2008b: 48). At the same time, West Germany not only gained a position in the world-market of plastics as in the world of product design (Waentig, 2008b). Nevertheless, this process was gradual and pejorative labels for plastics such as 'ersatz'[31] and 'artificial' had to be overcome by the general public (Waentig, 2008b: 84–95). The slogan 'there's no ersatz for plastics' was mentioned by F. Waentig as a reflection of that change towards the plastics image (Gäth, 1985: 48 as cited in Waentig, 2008b: 47). As stated by R. Lushington, in the 1960s, Germany stood out as one of the countries where plastics were accepted on a higher scale (Lushington, 1967). According to his testimony, 'plastics are regarded very differently in Germany to the way they are in the United Kingdom. There they are very much regarded as materials in their own right, rather than as substitutes' (Lushington, 1967: 99). From this, it can be concluded that during the late 1950s and 1960s industrial companies in Germany were able to benefit from a cultural, economic and social context that contributed to the promotion of plastics.
In relation to Bayer's history during this period, the company was going through a transition phase since it had just become independent from IG Farben.

> 'On August 17, 1950, the Allied High Commission passed Law No. 35, which laid down that what remained of I.G. Farben should be broken up into a number of economically viable, independent corporate units. These companies were to be autonomous in respect of both management control and ownership, thus promoting competition in the chemical and other related industries' (Verg, 1988: 314).

Thus, the Farbenfabriken Bayer Aktiengesellschaft was formed with headquarters in Leverkusen at December 19, in 1951, and in 1972 the name Bayer was adopted (Verg, 1988). From the moment of its independence, the main goal of Bayer was the recovery from war and from that, the conquest of the chemical market and its globalisation (Bayer AG, 2015). As previously mentioned, this reconstruction phase was 'linked with the Wirtschaftswunder, or "economic miracle", in the Federal Republic of Germany', and soon Bayer was conquering the trust of the United States (Verg, 1988; Bayer AG, 2015). Contributing to the company's expansion was Bayer's decision to invest in research (Bayer AG, 2015). Moreover, the further development of polyurethane chemistry was named by the company as one of the positive inputs for this demand (Bayer A.G., 2015).
Side by side with this will, the company recognized the necessity to conquer the consumer's trust in the new chemical materials. Since World War I, rebuilding the image of plastics was aimed by the industry and Bayer, due to its large market in synthetic polymer chemistry, was no exception (Waentig, 2008b; Verg, 1988). One example showing this will is the promotion of Bayer's materials at fairs.

[31] In F. Waentig's book, there is one explanation for the origin of the word 'ersatz'. 'The odium of the "ersatz" – the word has its origin in World War I and it is at that time, too, that the first, imperfect plastics made their appearance! – is a label that has long been attached to plastics and plastics products, not merely in their technical quality but also in the quality of their design' (Saechtling, 1955: 87 as cited in Waentig, 2008b: 92).

> At the International Plastics Fair in Düsseldorf in 1952, Bayer presented a light, soft foam that promised to be an ideal material for the upholstery sector. At the same time, Maschinenfabrik Hennecke exhibited a new kind of machine which manufactured this foam. Polyurethane foams had come of age (Verg, 1988: 319).

In design, this change of attitude towards plastics was mainly visible in the production of furniture. As stated by F. Waentig, in the 1960s 'designers took up plastics as a material and as a theme, integrating them into their work' (Waentig, 2012: 19).

In relation to polyurethane and as previously mentioned, this material played a particularly important role in furniture design. Bayer furniture fairs and most important, its 'living' programmes entitled *Visiona*, stood out as unparallel examples of furniture creations using PUR foams, TPU-based leathers and TPU fibres, among other synthetic polymers. In these fairs, Bayer's main goal was to show its newest developments in the fibres department, and aligned to that, to cement the consumer's trust in plastics and synthetic polymers. The fairs started in 1962 under the title *Wohnen Heute* ('Living Today') in parallel with the International Furniture Fair, in Cologne (Waentig, 2008b: 50); the motto 'Bayer's products of today for the houses of tomorrow' played a major role (Bayer, 1969: 22). To achieve these goals, Bayer looked at designers as its chance to get closer to consumers and most important, to enter into their homes. According to F. Waentig, 'Collaboration with designers was seen as a means of setting new aesthetic standards and of putting across in a visually effective fashion the technical possibilities as well as the practical application of artificial fibres' (Waentig, 2008b: 50). Still in her words, 'Designers were to play the role of intermediary between the manufacturer and the final consumer' (Waentig, 2008b: 50). Nevertheless, this demand was not only sought for artificial fibres. PUR, and especially foams, were one of the major big-name novelties of these fairs, especially in 1969 and 1970. Commonly used as a synonym of comfort, variability and flexibility, this material was used as a conquest tool for the public acceptance of plastics. Confirming the impact of PUR foams were the head titles *Schock in Schaum* ('Schock in Foam') and *Wohnen zwischen Schaumstoffdünen* ('Living between foam dunes') from the *Der Spiegel* of 1970 and 1972, respectively, which reported the tremendous success of this material during these exhibitions and the general impact of plastics in Germany (Wohnen, 1970: 149; Wohnen, 1972: 98). This acceptance started to become especially true when Bayer decided to hire the Danish designer Verner Panton (1926–1998) for the interior decoration of the white 'Dralon ship' as part of the International Furniture Fair programme (Waentig, 2008b: 50; Bayer, 1968). Panton seized the generous offer of the company and started to play with *Dralon* fibres and the many other material possibilities that Bayer had to offer, among them, polyurethane. For Verner Panton, to 'implement his vision of future living' and 'to question the whole basis of traditional habits of living' were his main goals (Waentig, 2008b: 50). Based on the closer work with Bayer's team, the successful liaison was undoubtedly achieved in *Visiona 0* (1968). Not only this triumph was materialised in the unique spaces of *Visiona 0*, as the 200 journals from more than 14 countries and

the circa 20 000 visitors that went to see the ship could confirmed it (Waentig, 2008b; Bayer, 1968: 6). Furthermore, the title *Visiona* was suggested by the designer and immediately adopted by Bayer (Waentig, 2008b: 50). From this, the 'Dralon ship' of 1968 was afterward named *Visiona 0* and in the following years, subsequent numbers were applied. Namely, *Visiona 1* was held in 1969 at the Interzum trade fair under the conception of the Italian designer Joe Cesare Colombo; *Visiona 2* took place in 1970 under Verner Panton's bold ideas; *Visiona 3* was planned by the French designer Olivier Mourgue in 1972, and *Visiona 4*, conceptualised by Jack Lenor Larsen in 1973.

The fairs were a tremendous success between 1968 and 1972 and the unique character of plastics was launched through the creation of new structures, shapes, forms, colours and patterns, but most of all, of new living programmes. The success of plastics in these fairs is clearly shown in the citation below.

> 'When the "Kunstsoff Rundschau" trade magazine looked back on the 1972 international furniture fair in Cologne, it wrote that plastics had finally come to be accepted. Synthetic materials were so well established and easily produced when making furniture that wood would ultimately be completely replaced' (Kunststoff-Rundschau, 1972: 71 as cited in Waentig, 2008b: 96–97).

Since F. Waentig's research work has already provided detailed information concerning *Visiona* exhibitions, hereinafter, each exhibition (from 1968 to 1972) is discussed through the unique point of view of PUR, following and highlighting the subsequent points:

- *Visiona 0*, 1968 (commissioned by Verner Panton): the entrance of PUR in Bayer furniture fairs;
- *Visiona 1*, 1969 (commissioned by Joe Colombo): the promotion of TPU-based artificial leathers and the assumed presence of polyurethane brands in the fair;
- *Visiona 2*, 1970 (commissioned by Verner Panton): the high point of the use of PUR foams in Bayer furniture fairs;
- *Visiona 3*, 1972 (commissioned by Olivier Mourgue): the globalisation of PUR-based designs to other countries and the importance of Bayer's *Visiona* exhibitions to the acceptance of plastics by the general public.

2.3.1 Visiona 0

One of the posed questions at the beginning of this research was why and how did Bayer invite Verner Panton for *Visiona 0*. Although their relationship has already been considered by F. Waentig, the decision-making process prior to this project has not been explored. For this, Bayer's in-house newspaper *Unser Werk* from 1968 proved to be an important source and a brief explanation was found (Bayer, 1968: 4). Along with Verner Panton, Bayer's Fibres department had also considered hiring

Professor Erna Hitzberger (from the Folkwang School, in Essen) for the Cologne Furniture Fair (Bayer, 1968: 4). As stated by Bayer, both 'artists' were known from long relationships with the company; Verner Panton from his 'residential hill' with Bayer's *Perlon*® fibres and Professor Erna Hitzberger from his experimental work with *Dralon* fabrics with his students (Bayer, 1968: 4). Nevertheless, although Verner Panton's ideas were bold, Bayer showed the courage to approve his plans and from this moment, Verner's 'living visions of tomorrow' took shape (Bayer, 1968: 5). However, due to the physical limits imposed by the ship, the implementation of Verner's plans was not an easy task and Bayer decided to commission decorators, furniture manufacturers and upholsterers to work side by side with Panton and Bayer's engineers (Bayer, 1968: 5–6). From this close collaboration between different specialists, Panton was able to ban the conventional notion of permanent facilities and to give shape to his new living programme that caused worldwide echo (Bayer, 1968: 6).

In relation to PUR, it could be said that *Visiona* exhibitions were materially paved by Bayer's recent developments in PUR foams, TPU fibres and coatings, along with acrylics, polyesters, PVC and polyamides. However, *Visiona 0*'s main goal was to focus on the promotion of Bayer's chemical fibres and, as a result, less attention was given to PUR possibilities. Still, the presence of this material was possibly confirmed in four objects, which due to their novel designs and clever use of PUR are discussed here: namely, the *Panton* chair, the hanging furniture seats entitled *Hanging Swing* (Fig. 2.9), the *Landscaped Interior*, and the multi-purpose seating *Living Cube*. These objects, probably produced for this occasion with PUR trademarks such as *Baydur*®, *Hartmoltopren*® and *Moltopren*®, consisted of remarkable examples designed by Verner Panton showing some of the most profitable advantages of PUR foams — strength, light weight and mould production. However, it is important to emphasise that this material ascription is not completely certain since the specific term 'polyurethane' was not found in the Bayer's issue from 1968. Instead, only the trade name *Hartmoltopren*® was found, which along with detailed close ups of *Visiona 0* exhibitions photographs, publications about Verner's work and the designer's prior work with Bayer, may justify this assignment.

> 'To Verner Panton there are only a few design elements in this residential/housing landscape. Traditional ideas of furniture are exiled. Combineable squares, inflatable balls, larger possibilities to seat, hanging furniture, hanging bowls made of ®Hartmoltopren, the seat height and comfort themself, living squares, which invite to sit, play, stand and lay, and finally pillows. Mountains of pillows, characterize this world created by him, still an unaccustomed world. Verner Panton, so they say, was many years ahead of his time. The most important expression in this Room landscape is for the artist the color: the color in its intensity, in its nuances. It primarily influences the human being who lives in it, determines his well-being, his strength and his actions. Thus the home textiles belong to the infinite and effective means of color, as if by themselves. They give the room the light, the coolness or warmth - the atmosphere' (Bayer, 1968: 6).[32]

[32] All translations found in this section were made by the author of this dissertation.

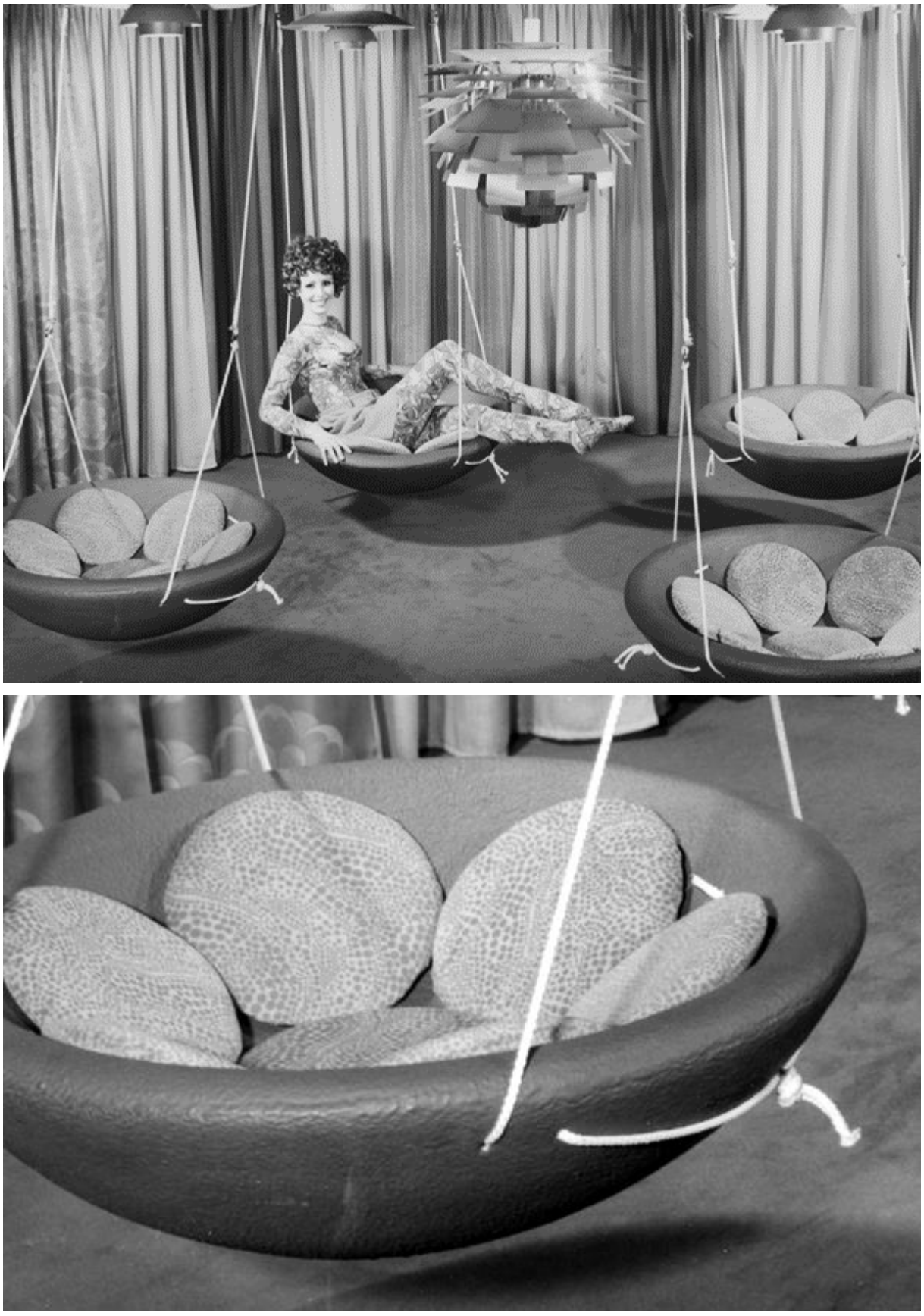


Figure 2.9 Verner Panton, *Hanging Swing*, design 1967 and production 1968 (above). Image from *Visiona 0* furniture fair, Cologne, 1968. Photo © Panton Design, Basel. Detail of the seat showing the typical texture of polyurethane rigid foams, in this case, the probable use of *Hartmoltopren®* trademark from Bayer (bottom).

Furthermore, both *Baydur*® and *Hartmoltopren*® were advertised by Bayer in the *New Scientist and Science Journal* in 1971 as PUR-based products. *Baydur*® was described as a 'versatile polyurethane', 'extremely easy to clean' and 'incredibly light' (Fig. 2.10, on the left) and *Hartmoltopren*® as 'a rigid polyurethane foam (…) more efficient than any other foam-based product' (Fig. 2.10, on the right). The specific product *Moltopren*®, although not found in the *Unser Werk* issue of 1968, was found in one Verner Panton's publication as a material used in *Visiona 0* (Vegesack & Remmele, 2000: 253, 257, 258) and defined by M. Alger as 'an early flexible polyurethane foam' (Alger, 1997: 323).

Figure 2.10 Baydur® advertisement from the *New Scientist and Science Journal*, 1971 (left) (Bayer, 1971: 494). Hartmoltopren® advertisement from the *New Scientist*, 1971 (right) (Bayer, 1971: 138).

The *Unser Werk* issue from 1968 also described the high value given to comfortable, soft and flexible cushions, which highlights the increased importance given to foamed materials. The section was entitled *Kissen machen Karriere* (translated to 'Pillows make a Career') and was followed by the motto *Alle Ruheprobleme lassen sich durch Kissen lösen* ('All your silent problems at night can be solved by pillows') (Bayer, 1968: 6).

Regarding the promotion of the materials used for *Visiona 0*, yet another question can still be posed. How did Bayer and Verner Panton plan to communicate these novel materials to the public? Was the public aware of commercial trade names, properties, suppliers and advantages of each material? How was the industrial knowledge transferred to the main user? These questions, often put aside from the

main topics focused on in the specialised literature, are considered in this chapter. As stated by the Bayer sales department in the *Unser Werk* issue of 1968, the trade fair visitor was able to look at each individual material and evaluate their weigh, texture and feel; and each material had a number that could be used to identify the name and address of the material manufacturer. Therefore, the public was aware of the properties of each material and conscious of its manufacturer.

At the end, Bayer described *Visiona 0* as a fascinating coloured world between dream and reality (Bayer, 1968). Panton's living model was such a success that the most beautiful rooms of the *Dralon* ship were then exposed for several weeks in the Louvre (Paris), alongside Joe Colombo and Roger Tallon designs. Due to the positive effect of *Visiona 0*, Bayer announced a future exhibition with Verner Panton to take place in January, in 1970 (Bayer, 1969: 22).

Nevertheless, the time spent between 1968–1970 could not be wasted and in 1969, Bayer decided to commission Joe Colombo for *Visiona 1* (1969), held at the Interzum international exhibition centre (Bayer, 1969: 24).

2.3.2 Visiona 1

For this occasion, Colombo created three housing elements that aimed to determine the face of the house of the future — the 'living-centre', the 'night-cell' and the 'kitchen-box' (Bayer, 1969: 25). For this, Bayer's material concept was larger and as stated by F. Waentig, Colombo 'started out from a model in which all the new technical possibilities in the plastics field were to be exploited' (von Vegesak, 2000, 168 as cited in Waentig, 2008b: 50). In accordance with this, Bayer's 'Unser Werk' issue from 1969 announced the motto 'Bayer's products of today for the houses of tomorrow' (Bayer, 1969: 22) and the application of the commercial PUR products *Vistram®*, *Hartmoltopren®*, *Moltopren®* and *Dorlastan®* (Bayer, 1969: 22–30). This may emphasise the increased knowledge and diffusion of PUR products through the public as well as Bayer's wish of to extend its furniture fair to other materials than acrylic and polyester fibres.

Among the whole set of publicised materials in *Visiona 1*, *Vistram®* was definitely the novelty most announced in this 'Unser Werk' issue. This 'polyurethane-coated material' which is 'breathable, it does not stick, no heat accumulates and is pleasantly dry to the touch' (Bayer, 1969: 29) was mentioned in this issue almost thirty times in nine pages (Bayer, 1969: 22–30). The sentence 'Wenn es um moderne Wohngestaltung geht, dann hört man immer häufiger das Wort ®Vistram' ('When you think about modern lifestyle, you hear more and more often the word ®Vistram') reflected that importance (Bayer, 1969: 28). From this material, Joe Colombo constructed the flexible wall (concertina wall) around the night-cell and with that, separated it from the living centre (Fig. 2.11). *Vistram®*, due to its modern, bright, supple and shiny look, was selected by Colombo as an advantageous option for the construction

of his 'living machine' (Bayer, 1969: 25). In this way, his idea of a residential model achieved by the conjunction of individual parts was possible and PUR was part of that vision (Bayer, 1969).

Figure 2.11 Joe Colombo, night-cell showing the concertina wall made of *Vistram®*. Image from *Visiona 1* furniture fair, Cologne, 1969. Photo © Bayer Corporate Archives.

According to H. Träubel, *Vistram®* was the first artificial polyurethane-based leather in the final sixties (Träubel, 1999). Moreover, this material was considered 'flexible and abrasion resistant and adhering dirt was easy to remove' (Träubel, 1999: 257). Still in line with Träubel, not only this leatherlike product paved its way in furniture, as it was a successful material to be used in shoes, clothing and bags. Nevertheless, its composition based on diethylene glycol adipate ester led to a lower resistance to hydrolysis and, later, to the rise of claims from customers shortly after two to three years of its commercial sale (Träubel, 1999). As a result, 'Articles made of Vistram were only in use for a short period' (Träubel, 1999: 257).

On the other hand, since this material was giving its first steps in the market of artificial leathers in 1969, Bayer looked at *Visiona 1* as the opportunity to launch a great promotion campaign for *Vistram®* (Bayer, 1969). Among several publicity efforts, Bayer called for journalists and company members from Germany and abroad to get in touch with the wide range of materials offered by *Vistram®* (Bayer,

1969). Moreover, the visitors were able to sit on *Vistram®* sofas and confirm the good properties of the material, as well as to verify the easiness of dirt removal from the surface of these leathers (Bayer, 1969). The slogan *Auf Vistram-Polstern sitzt man angenehm* ('On Vistram cushions you sit pleasantly') found on Bayer's 'Unser Werk' issue from 1969 was found as a promotion tool for this product (Bayer, 1969: 29).

Besides mentioning these polyurethane leatherlike products, this same document also reported a TPU fibre with the trade name *Dorlastan®* (Bayer, 1969: 26). The assignment confirmation of this trade name to a TPU product was only possible with the access of the 'Polymer Science Dictionary' by M. Alger, where *Dorlastan®* was described as a polyurethane elastomer showing 'good wear properties, high strength and excellent oil and solvent resistance' (Alger, 1997: 72). In this way, the already acknowledged wide range of products offered by polyurethane during this period was reinforced through the indirect testimony of Bayer manufacturer in its in-house newspaper.

2.3.3 Visiona 2

For *Visiona 2* in 1970, Verner Panton was once more commissioned by Bayer but this time, to show the most audacious and unexpected design ideas that plastics and fibres could offer. Although again restricted to the Rhine steamer, Panton launched his 'model for tomorrow's living' (Waentig, 2008b: 51) without thinking of walls or on the traditional concepts associated to living rooms and apartments (Bayer, 1970). Bayer's and Verner's motto in this year differed from 1968 in the way that 'the courage to experiment' was selected as the motto of all steps involved in the creative processes (Bayer, 1970: 22). These words, also the title of one section from the 'Unser Werk' 3/70 issue, were particularly selected to highlight the current reality that plastics had brought (Bayer, 1970). In other words, more and more synthetic materials demanded the courage of designers, architects and the industry, as Bayer and Verner showed in *Visiona 2* (Bayer, 1970).

Nevertheless, although the living programme of *Visiona 2* was proposed as a 'Tomorrow's reality', Bayer made clear that this future could be applied right away, since these ideas can be already realised from its materials (Bayer, 1970: 22). However, due to the novelty of these products, their processing into bold designs was not an easy task and a long road was paved. For that, Bayer mentioned the teamwork spirit during the preparation of *Visiona 2* as well as the unusual knowledge of Verner Panton on synthetic materials and technical aspects involved in their processing (Bayer, 1970: 27). Therefore, not only this close partnership has resulted in the outstanding showroom that was *Visiona 2*, as Bayer was able to improve some of its own materials and develop new ones (Bayer, 1970: 27).

Concerning the materials applied, PUR was particularly used in *Visiona 2*. As flexible foams, the famous *Phantasy Landscape* (1970) (Fig. 2.12), the *Weave* 3D carpet (1970), the *3D-Programme* (1969/70), the *Cloverleaf-Sofa* (1969/70) and the waterproof bathing sofa[33] are examples of such use.

Figure 2.12 Verner Panton, *Phantasy Landscape*, 1969/70. *Moltopren®* foam and *Dralon®* fabric Image from *Visiona 2* furniture fair, Cologne, 1970. Photo © © Panton Design, Basel.

As rigid foam, the *Pantoffel* recliner (1969/70) (Fig. 2.13), and the blue table (1969/70) can be named. To this end, trade marks such as *Moltopren®* (PUR flexible foam) and *Baydur®* (varnished PUR high-resistance moulded product) were selected.

The bet on PUR foams by the German plastics industry was becoming so successful that few days earlier of *Visiona 2* opening the *Der Spiegel* ceded one of its pages to the announcement of this exhibition.

[33] At first, Panton´s wish to fill the bathing sofa with water was viewed by Bayer experts as a completely senseless idea. Nevertheless, after some headaches, Panton's wish was granted and the use of PUR foam (*Moltopren®*) and polyamide fibres (*Perlon®*) resulted in the object shown in Fig. 2.33.

Figure 2.13 Verner Panton's design with *Baydur*®: *Pantoffel* recliner, 1969/70. Image from *Visiona 2* furniture fair, Cologne, 1970. Photo © Bayer Corporate Archives.

In the *Der Spiegel* article, PUR foams were described as the material for the most avant-garde interior designers, along with the example of the *Living Tower* seating (1968/1969) by Verner Panton (Wohnen, 1970: 149). This furniture object is part of the MUDE collection.

From the large set of objects from *Visiona 2*, there is no doubt that PUR (mostly foams) provided an outstanding revolution in furniture design, to which the giant manufacturer Bayer showed the talent to benefit from. This fair was such a success that more than 80 000 visitors went to see Verner Panton's interior design and circa 24 000 visited the fair during the four days (Bayer, 1970). According to Bayer's opinion, *Visiona 2* not only had 'led to new developments as also drawn the boundaries from which certain materials are set' (Bayer, 1970: 27). PUR, among this set of materials, was definitely one of the most explored in all its technical and design potentials by both Bayer and Verner Panton. On the other hand, the work of Bayer with designers did not stop with Verner, and in 1972, the *Visiona* concept continued under the leadership of the French designer, Olivier Mourgue (Bayer, 1971).

2.3.4 Visiona 3

Although Olivier Mourgue's design work was already famous for the *Djinn* series produced by the French company Airborne (France), for the occasion of *Visiona 3*, his intention was different. According to an interview for the American magazine *Industrial Design* in 1968, O. Mourgue explained that he was in quest of an opportunity to free himself from the label of 'furniture designer' attributed to him during his work with Airbone (Mourgue as cited in An interview, 1968: 44). As stated by the designer, 'It is very hard in this country to remove the impression that one is strictly a furniture designer once that impression has been given' (Mourgue as cited in An interview, 1968: 44). In this way, Bayer's invitation to Olivier Mourgue could be imagined as a long-wished opportunity and therefore, Visiona 3 started to be planned. For this fair, the concept was different and the space was filled by all shades of greens through the motto 'Back to Nature' (Bayer, 1972: n.p.; Bayer, 1971). Mourgue replaced walls by movable curtains, designed a soft bay resembling earth and grass and created a fluffy white carpet that offered relaxation (Bayer, 1971: 12). To produce this living project, once more the teamwork spirit was mentioned by the company (Bayer, 1972). Bayer´s singular synergetic work with famous international designers was a crucial part of Visiona's programmes and definitely, one of the main reasons for their success.

In relation to material proposals, among a wide range of home textiles and furniture items made of *Leguval®* and *Novodur®*, *Baydur®* and *Moltopren®*, PUR was once more used in this exhibition (Bayer, 1972: n.p.). Nevertheless, no particular PUR-based furniture was highlighted in the *Unser Werk* issue of 1972. Instead, the careful analysis of *Visiona 3* video allowed identifying the *Bouloum* chair, in green and white colours, which was probably produced with PUR moulded foam. This chair, although firstly produced by the French company Airbone, was licensed to Arconas Corporation (Canada) since 1978. Curiously, during this research, the work of this company was found to be discussed in the section 'Industry News' of the *Journal of Cellular Plastics*, in 1987 (Good Design, 1987). In this journal, John W. Neufeld (president of the Arconas Corporation), mentioned the production of the *Bouloum* chair with cold-cure-moulded high-resilience (HR) PUR foam supplied by Mobay Corporation, one of Bayer's USA Inc. companies.

> '"Our designers use the Bayfit 550 urethane foam system as a kind of chemically engineered time machine," Mr. Neufeld said. "It gives them the creative latitude either to research the past, explore present trends, or visualize what might happen tomorrow – sometimes to do all three" – he added' (Neufeld as cited in Good Design, 1987: 533).

This journal article enabled to confirm the international growth of Bayer's PUR industry outside Germany and the global spread of *Visiona 3* designs. In this case, the *Bouloum* chair designed by Olivier

Mourgue (Good Design, 1987: 533). This object was mentioned as being produced based on a 'Foaming-to-Shape' process, which resulted in twice denser foams (Good Design, 1987: 533). According to the designer Conrad Marini (president of CMM Design Associates and part of Arconas' team), these polyurethane systems were irreplaceable.

> '"The creative potential of HR urethane foam is relatively unexploited," Mr. Marini asserted. "The system gives designers the freedom to shape a fluid material, so the furniture actually flows through space and paradoxically, through time. Nothing I can think of, or dream of, can replace it as a design material," he emphasized' (Marini as cited in Good Design, 1987: 534).

From this statement, we may look at PUR as a highly appreciated material for designers, industrialists and consumers, and to which both scientific and weekly newspapers such as the *Der Spiegel* were paying attention. In a day before the opening of *Visiona 3*, the title 'Living between foam dunes' was heading the 'Kultur' section of the *Der Spiegel* (Wohnen, 1972: 98). The *Dana* mattresses by Femira, the *Siesta* beanbags by Rolf Benz (Fig. 2.14) and the *Phantasy Landscape* by Verner Panton are referred to in this article.

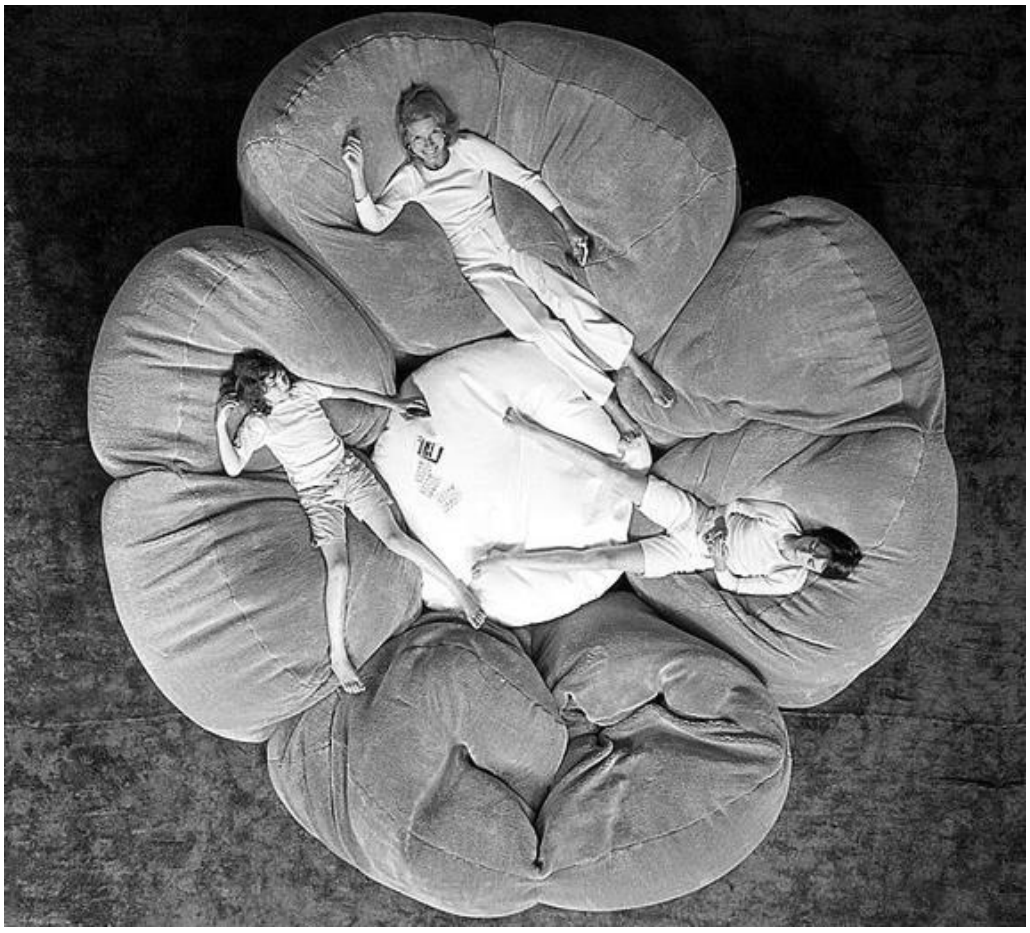


Figure 2.14 The *Siesta* bean bags produced by Rolf Benz. Image from the Furniture Fair, Cologne, 1971 (Rolf Benz, n.d.).

In general, it is possible to conclude that the popular status of foams as popular materials in furniture and interior design was rising in Germany. Consequently, PUR was more and more a clearly accepted material by the public. From this synthetic polymer, Bayer and other German companies (such as BASF) created living concepts through in-house developments that have become worldwide recognised through Visiona and other International Furniture Fairs.

Still, Italian companies such as Gufram and Poltronova have also contributed to take polyurethane into the houses of consumers during the 1960s and 1970s, as discussed in the following section. They were also responsible for showing how this polymer can be worked into complex forms that recall for playful spirits and experimentalist characters.

2.4. Two important case studies from the Italian landscape – Gufram and Poltronova

The work of Italian companies such as Gufram and Poltronova cannot be left aside from this research, because these companies have been recognised for their unique and singular work with PUR foams, as seen in the MUDE collection with its high number of Gufram and Poltronova productions. Consequently, this section intends to give new insight into the work with this material of these important companies. Firstly, the information already published is reviewed, followed by discussion of testimonies collected through written questionnaires planned during this research and focused on the entrance and use of PUR by the two firms.

Concerning the first point, Italy was frequently addressed as a particular case of design during this period. Critics, historians and designers such as Stephen Paul Bayley, Philippe Garner (Bayley *et al*., 1986), Penny Sparke (1988), Kjetil Fallan, Grace Lees-Maffei (Lees-Maffei & Fallan, 2014), Andrea Branzi (1984) and Emilio Ambasz (1972), among others, have stated that Italy was 'the dominant force in consumer-product design' during this period (Ambasz, 1972: 19). Chapters and books entitled '"The Good Life": designing the Italian Miracle' (Sparke, 1988: 121–159) and 'The hot house: Italian new wave design' (Branzi, 1984), along with expressions such as 'Made in Italy' (Fallan, 2009: 257), 'Italy as the "home of design"' and the 'Italian look', also support this statement (Baroni, 1978 as cited in Sparke, 1988: 131). In relation to the use of novel materials such as plastics and other synthetic polymers, Penny Sparke has also described Italy as 'the first country to find a truly modern idiom for plastic' (Sparke, 1988: 169). Nevertheless, how has Italy gained this status in design? According to the historian Kjetil Fallan, Italy has also benefited from the prosperous economic growth of the post-war period, which has resulted from financial incentives of the *Marshall Plan*, the formalisation of new trade agreements, the changes in the industrial structure of Northern Italy and the increased migration

to industrial centres (Fallan, 2009). In his words, 'The considerable growth of private consumption and industrial output, combined with a rapid development of production technology, would have a strong impact on the upcoming changes in Italian industrial design' (Fallan, 2009: 258). From this, a consumer society started in Italy during the 1950s, 'aspiring to consumer products for the domestic scene and leisure activities' (Fallan, 2009: 258). Thus, 'The mid-1950s can be said to be a turning point in the consolidation of industrial design in Italy' (Fallan, 2009: 259). Along with the appearance of design magazines (e.g. Casabella, Domus, and Modo), associations and international exhibitions (e.g. the Triennale di Milano), Italian industrial design started to pave every aspect of modern living, becoming a major force in the Italian society of the 1950s. In addition, Italy's design was gaining such prominence in this period that in 1972, the Museum of Modern Art, (MoMA, New York) dedicated an entire exhibition to this subject, entitled *Italy: The New Domestic Landscape: Achievements and Problems of Italian Design*, curated by Emilio Ambasz (Ambasz, 1972). In this exhibition, both Gufram's and Poltronova's design productions were shown, along with the work of more than 100 designers from the last decade in Italy (Ambasz, 1972). According to the introductory text in the exhibition catalogue, the force of the Italian design was not limited to country boundaries or to stylistic issues.

> The Italian design 'has influenced the work of every other European country and is now having its effect in the United States. The outcome of this burst of vitality among Italian designers is not simply a series of stylistic variations of product design. Of even greater significance is a growing awareness of design as an activity whereby man creates artifacts to mediate between his hopes and aspirations and the pressures and restrictions imposed upon him by nature and the man-made environment that his culture has created' (Ambasz, 1972: 19)

In this way, more than the production of tangible products, the Italian design force can be characterised by an intellectual debate (recognised in Europe and worldwide) about the purpose of design in the cultural society of the 1960s and 1970s. This debate, according to P. Sparke, emerged from the loss of cultural and sociological values in design in the late 1960s. Although Italian goods were successfully marketed at an international level, 'within Italy itself, on an ideological level, design experienced a severe crisis' (Sparke, 1988: 182). As cited in her publication, the primary role of Italian design was being 'replaced by an empty formalism which came to symbolize nothing other than the commercial and consumeristic values associated with advanced capitalism' at the end of the sixties (Sparke, 1988: 182). Therefore, it was necessary to rethink its purpose, which according to E. Ambasz, gave rise to two different programs presented on the exhibition: Italian design "objects" and commissioned environments (Ambasz, 1972). The objects were categorised into three different visions: the Conformist, the Reformist and the Contestatory; the environments were divided among design as postulation, design as commentary and counterdesign as postulation (Ambasz, 1972). The

radical (or the anti-design movement) was also represented in this exhibition. In the words of P. Sparke, the radical design intended 'to negate the idea than an object's aesthetic function is more significant than its more abstract socio-cultural role' (Sparke, 1988: 185). Some Gufram's and Poltronova's productions are representatives of the Italian radical design, mostly due to the 'provocative, witty and eccentric' characteristics of their creations (Bayley *et al.*, 1986: 262–263). Nevertheless, the understanding of this movement requires the understanding of other artistic references. Apart from the object debate as a mere server of aesthetic and utilitarian functions, the Pop movement from America and Great Britain has been mentioned in the literature as an influence of the Italian radical design (Sparke, 1988; Bayley *et al.*, 1986)[34]. According to Bayley *et al.*, this influence may have come from international exhibitions such as the *Venice Biennale* of 1964 (which showed important artworks of the Pop Movement) (Bayley *et al.*, 1986: 262) as well as from Ettore Sottsass travels to London and New York.

> 'Sottsass travelling the world for Domus. To him Domus owes an endless number of signals, signals from far away. The first signals of Pop Art from New York — how many years ago? — arrived from him, signals that were already critical, foreseeing the coming entropy…' (Ponti, 2013: n.p.).

As examples of Italian designs evoking inspirations on Pop, Gufram's and Poltronova's productions can be named. According to Bayley *et al*., this influence can be seen on the encouragement of 'designers to exploit vulgarity, brashness and bright colour, and to use synthetic or disposable materials in contexts in which they would formerly have been unacceptable' (Bayley *et al.*, 1986: 249).

Moreover, and due to the cultural debate paved in Italy, important radical design groups emerged during this period (Sparke, 1988). Among them, Archizoom Associati (1966–1974, Firenze), Superstudio (1966–1978, Firenze), Studio 65 (1965, Turin) and Gruppo Strum (1963, Turin), which were part of Gufram' and Poltronova's history. Another imperative name was Ettore Sottsass Jr., also known as 'the father figure' of the radical design movement (Bayley *et al.*, 1986: 262) and the artistic consultant of Poltronova from 1957 onwards. In this way, the relevance of these companies in the historical framework of Italy's radical design is undeniable, as well as the importance of designs such as *Pratone*, *Capitello*, *Bocca*, *La Cova* and *Joe. Pratone* and *La Cova* due to their natural appearance and use of artificial materials (see Appendix III), *Capitello* due to its neoclassical taste and Pop attitude (see Appendix III) and *Bocca* and *Joe* due to their relationship to Hollywood and baseball stars (see Appendix III). In general, all these pieces reflect the critical spirit of the Italian designers during this period[35].

[34] However, it should be taken into consideration that the influence of the artistic Pop movement in the Italian design was not explored in depth during this research. Therefore, opposite influences should be considered as well.

[35] Although this study does not intend to go deeper into the complexity involved in the study of Italian radical design, its multifaceted socio, political and cultural aspects were acknowledged and additional Italian authors may be mentioned as

From the access to exhibition catalogue and records from The Museum of Modern Art, several PUR-based objects were recognised to be held at the exhibition *Italy: The New Domestic Landscape* (Ambasz, 1972: 26–133; Italy: The New, n.d.). Besides Gufram and Poltronova, other companies and designers (Table 2.1) were using PUR to materialise design theories and positions, crossing the three Italian tendencies presented by E. Ambasz at MoMA in 1972 (Ambasz, 1972: 26–133). For these objects, flexible foams, self-supporting polyurethane (probably rigid foam) and TPU-based leathers were the polyurethane forms mostly used (Ambasz, 1972: 26–133). From Table 2.1, PUR can be recognised as a highly appreciated material by Italian furniture companies during this period; not only it was used by radical designers due to the unlimited design potentials of the material, as its used was observed for mere aesthetic and utilitarian purposes.

Table 2.1 Italian polyurethane-based objects shown in the exhibition, *Italy: The New Domestic Landscape*, in 1972

Author	Company	Object
T. and A. Scarpa	Cassina	*Ciprea* armchair (1968); *Soriana* lounge chair (1970)
R. Bonetto	Flexform	*Boomerang* lounge chair (1969)
C. Boeri	Arflex	*Bobolungo* lounge chair (1969)
G. Pesce	C & B	*UP* series (1969)
S. Mazza and G. Gramigna	Cinova	*Poker* demountable chair (1970)
U. Catalano and G. Masi	NY Form	*Ghiro* mattress-lounge chair (1967)
J. De Pas, D. D'Urbino and P. Lomazzi	BBB Bonacina	*Galeotta* lounge chair (1967)
S. Matta	Gavina	*Mallite* combinable seats (1966)
J. Colombo	Flexform	*Tube* chair (1969)
	Sormani	Additional System lounge chair (1968); *Multichair* (1969)
A. Castiglioni	Zanotta	*Primate* bench (1970)
A. Becchi	Giovanetti	*Anfibio* couch (1971)

Texts reflecting the tremendous success of the Italian design in New York and the use of PUR in furniture design have been found on articles and notes from American magazines with the headings 'Moma Mia, That's Some show' (Reif, 1972: 41), 'Rock and Droll' (Rock, 1974: 54) and 'Foam Furniture

based literature for the subject: Catharine Rossi, Raimonda Riccini, Renato De Fusco, Vittorio Gregotti, Maddalena Dalla Mura and Carlo Vinti

Rises Like Bread' (Foam, 1970: 25). From these articles, PUR-based objects were identified as well as the sentence, 'This is audacious thinking, industrialized thinking that goes far beyond today's mobile homes and tract housing' (Reif, 1972: 41). Consequently, the unique use of PUR foams by Italian designers was worldwide successfully appreciated. Nevertheless, in relation to personal testimonies justifying the reasons that led these designers to choose PUR over other materials nothing has been found. To this end, scripts interviews to interview Poltronova and Gufram were specifically designed during this research (see Appendix II). This approach enabled to expand the current knowledge about their work with PUR and to answer to the following questions: How did they first know about the existence of PUR? Why did they start to use it? How was their aesthetic and material experience with this material? What were the advantages and disadvantages? How was the creative process? and finally, how did they relate to the ephemeral nature of PUR (if considered). This way, two important testimonies were collected and due to the precious information enclosed in the produced records along with the valuable collaboration of the interviewers, relevant and new information was produced. However, due to different interviewing approaches, one by email and the other by phone, the detail level of the responses was different. Even so, precious information was collected and produced. From Gufram, the whole set of questions was answered by Axel Iberti, the Head of Product Department and from Poltronova, by Roberta Meloni, the President of Centro Studi Poltronova, both in March 2014.

According to Axel Iberti, Gufram was founded by the Gugliermetto brothers in Turin, in 1966, from the name 'Gugliermetto Fratelli Mobile' (A. Iberti, phone interview, March 21, 2014). In his words, the company 'was born from polyurethane', i.e. the Gugliermetto brothers created Gufram with the exclusive intention to work with this versatile polymer. Starting as founders of an artisan firm dedicated to furniture production and upholstery in 1952, both brothers were familiar with PUR forms and suppliers. From this, they decided to devote they entire attention to this material and in 1966 created a 'design laboratory' committed to furniture items based on PUR, called Gufram. In this way, PUR can be regarded as a unique material that due to its unlimited potentials in design was capable of catching the attention of two industrials, leading them to bet everything on a single material. Nevertheless, although Gufram owned its own design laboratory, Iberti highlighted that Gufram did not synthesise any form of this material. Instead, PUR formulations were acquired from well-known manufacturers such as Bayer and Dow. Raimondi, known for his fondness for design experiments and research into new and expressive materials (such as PUR), became the creative director of Gufram in 1966 up to 1970 (Gufram, n.d.). According to Iberti, the beginning of PUR productions started with him and more specifically, with the *Alvar* chaise-longue, in 1967. So, Gufram's journey with PUR has started. However, a question can still be posed. What did Gufram founders and designers see in PUR? According to A. Iberti, PUR has always been a requisite of Gufram and a well-known material for the founders since the 1950s. As a result, although Gufram has always worked in collaboration with

designers and artists coming from Italy Architecture schools, their main goal was to invite them to the laboratory to experiment with PUR and possibly, to create other new materials (A. Iberti, phone interview, March 21, 2014). As mentioned by Iberti, Piero Gilardi's famous Guflac® finish is one of the most successful outcomes of that freedom of creation and experimentation in the company. He mentioned the *Pratone* lounge chair as a project that took five years to be executed. Therefore, playing with materials was Gufram's main priority. Regarding PUR, this material was described as one of the few material examples that allow such quality. As stated by Iberti, PUR 'enabled to create something original and unique, bringing together beauty and lightness'. Furthermore, 'polyurethane along with Guflac® were the only materials allowing to reach this goal' and 'the creative processes have always started from the material, always from polyurethane'.

On the other hand, several drawbacks were also reported by Iberti and concerning to polyurethane, the technical features associated to mould production were mentioned. According to his testimony, 'polyurethane is not an easy material, it requires a real technical attitude' and 'it is important to be aware of its application limits as well as of the advantages that can be drawn from its use'. In the opinion of Axel Iberti, Gufram differs from other companies by its unique work with the combination of PUR and Guflac® which in short, was the result of a truly experimental attitude, closer to designers. In contrast, Poltronova's attitude towards polyurethane was different. In this case, the main focus of the company was not to work exclusively with this material but to bring new forms and technologies to homes (R. Meloni, written interview, March 23, 2014). As described by Meloni, Poltronova was founded by Sergio Cammilli in 1957, in Tuscan, Pistoia, along with other craftsmens and upholsterers. Nevertheless, it was with Ettore Sottsass Jr. that Poltronova renewed its furnishing. According to Meloni, the early years of Poltronova's design production (1957–58) were mostly paved by an inspiration in Scandinavian design, mainly, due to the traditional work of the talented artisans from Tuscan. Nevertheless, in 1958, Sergio Cammilli attended the Art Institute and immediately met Ettore Sottsass. From this moment, a real design strategy for Poltronova has started. Similarly to Gufram's team, PUR was also a well-known material for Poltronova, in this case, due to the work of Italian companies such as Arflex (Milan) and its PUR-based furniture; and Pirelli S.p.A., and its 'the so-called Pirelli's foam which was like a Swiss cheese', as mentioned by Roberta Meloni. The beginning of the polyurethane journey in this company started with the *Superonda* sofa by Archizoom Associati, in 1966 (Fig. 2.15). Although known as one of the first sofas without a conventional frame, the creative process of *Superonda* started in 1966 as a wooden block that was part of the exhibition 'Superarchitettura'. This exhibition, presented by Archizoom Associati and Superstudio in Pistoia, was marked by coloured, vibrant and bright objects, close to the Pop art movement. As stated by R. Meloni, the 'Superarchitettura' exhibition was the starting point of a new era for Poltronova. According to her, Cammilli, 'always attentive and very close to avant-garde art', went to see the show, met the young

authors and decided to produce the sofa. Nevertheless, R. Meloni alerted for the fact that Archizoom members were not familiar with polyurethane, or with its technical requirements (R. Meloni, written interview, March 23, 2014). Therefore, final design adjustments were carried out at the company as well as density tests to determine the suitable density for the PUR foam.

Figure 2.15 Archizoom Associati, *Superonda* sofa, 1966. Polyurethane foam and synthetic leather cover. Image from the catalogue of Centro Studi Poltronova, 2016 (Centro Studi Poltronova per il Design, 2015: 65).

For Cammilli, PUR foam has been seen as a soft but at the same time, structural material. It allowed new forms, various degrees of density and it was light. In general, this new polymer gave the possibility to design 'removable', 'washable' and 'replaceable' sofas and armchairs and in this way, surpassed the

old methods of padding (R. Meloni, written interview, March 23, 2014). For moulded pieces, the production method was recognised to be more difficult, requiring high technical support and investment in time and money. Following this production were the *Joe* armchair in 1970 and the *La Cova* nest in 1973. However, only PUR allowed to produce such furniture items with these novel shapes and low weight.

In summary, although for both companies, designers and artists were invited and polyurethane was used to produce bold design ideas, each company defended a different creative process. In Gufram, the whole set of projects started from experiments with the material, while for Poltronova drawings were the first step and only then the best materials were sought. Regarding disadvantages concerning the use of PUR, different testimonies were collected. Whereas for Gufram the ephemeral nature of PUR was recognised but not considered as a negative aspect, i.e., non-limiting (A. Iberti, phone interview, March 21, 2014), for Poltronova, and because the testimony was collected from the President of the company's archive, a different perspective was reported. Although she has not mentioned any disadvantage possibly mentioned by designers (besides the technical requirement of moulded processes), the loss of elasticity of PUR upon ageing and its tendency to become stiffer and crumble were stated. Nevertheless, this material continues to be used by both companies in re-editions of these objects, as well as in new design projects. Moreover, during the interviews, none of those interviewed mentioned any other polymer that could have been used instead of the PUR foam. Therefore, it may be concluded that for these two Italian companies the image of PUR as a highly appreciated design material is preserved, surpassing future conservation issues that may rise from its physical and chemical properties.

Still, the knowledge about the use of this polymer in the Portuguese context remains entirely absent. Consequently, the following section is entirely focused on national production and the use of PUR during the 1960s and 1970s.

2.5. The Portuguese landscape

At the beginning of this investigation, the dearth or total void of knowledge concerning the historical framework of Portuguese PUR industries was recognised. Nevertheless, this lack of information was not unexpected, given the general (national and international) scarcity of studies exclusively dedicated to plastics biographies, as previously reported.

On the other hand, the research work conducted by Maria Elvira Callapez has been countering this research tendency in Portugal. From her Master's and PhD researches, the titles 'Os Plásticos em

Portugal'[36] (Callapez, 2000) and 'História do PVC em Portugal'[37] (Callapez, 2010) were published, which can be regarded as the first publications where the national history of plastics was thoroughly studied. More recently, the conservator researcher Sara Babo has been focusing on the particular development of PMMA industries in Portugal (Babo *et al*., 2015). Besides these few references, three national bulletins from 'Plásticos: revista da indústria de matérias plásticas' (industrial periodical published between 1967–1978) (nº 4, 13 and 21) and four national bulletins from 'CNP plásticos: boletim informativo' (industrial periodical published since 1978) (nº 9, 23, 26 and 28) were added. Nevertheless, processing industries working with PUR were rarely mentioned in these documents, leading to the idea that this industry was poorly established in Portugal during the 1960s and 1970s.

In what concerns the history of Portuguese design, more references were found. José Augusto França, Victor Almeida, Maria Helena Souto and Carlos Duarte have focused some of their studies on the history of Portuguese design between 1960–1974 (Almeida, 2009; Souto, 2013, Duarte, 2001; França, 2004); João Paulo Martins, Ana Rato and Maria Helena Souto on the specific work of the Portuguese designer Daciano da Costa[38] (Martins, 2001; Souto, 2001; Rato, 2002); Graça Pedroso on Portuguese furniture during this period (Pedroso, 2009); and finally, Victor Almeida, Fernando Seixas (industrial entrepreneur) and Maria Otília Lage on the singular work of the Portuguese furniture company, Metalúrgica da Longra (Seixas, 1971; Lage, 2010). Similarly to the previous case, additional references were added and national periodicals exclusively dedicated to design and architecture were included, namely, 'Arquitectura' (1927–1984) and 'Binário' (1958–1977). In sum, these and the previously mentioned references constituted the base-literature for the historical contextualisation and state of the art of this section.

To our knowledge, this section might be the first study concerning the entrance of PUR industries in the country of Portugal as well as the national production of furniture design with this material. Since iconic Portuguese case studies (1960s–1970s) showing PUR (see Appendix III) are represented in the MUDE collection and the development of the PUR industry in this country have not been focused in the literature, the urgency involved in this study was clear. It was observed that although these objects (from MUDE) have been attributed to important national furniture companies such as FOC – Indústria de Mobiliários e Equipamentos, S.A., (1930–?, Mafra) and Metalúrgica da Longra (1920–1993, Longra), information concerning the objects' materials and the motivations that led Portuguese designers to choose PUR over other options was lacking. Consequently, the fulfilment of this gap has been achieved by this study.

[36] 'Plastics in Portugal'. All translations found in this section were made by the author of this dissertation.

[37] 'History of PVC in Portugal'.

[38] Daciano da Costa is considered a leading figure of Portuguese design as well as one of the supporters of design as a professional activity in the country.

This section starts by reviewing briefly the research work conducted by the authors cited above and follows with the presentation of the results collected during the investigation about PUR industries in Portugal and their influence on the production of Portuguese design with PUR.

According to M. E. Callapez, the introduction of plastic industries in Portugal took place in the 1930s (with Bakelite) (Callapez, 2000). For this entrance, two national conditions played a major role: the wish of the Portuguese government to renovate its industrial sector and the urgency of the country to get closer to what was happening abroad (Callapez, 2000). However, additional economical and historical factors have also contributed to this desire: (i) the *Wall Street Crash* of 1929; (ii) the national implementation of *Regime do Condicionamento Industrial* (an effective system for industrial protectionism) in 1931; (iii) the opening of the *Grande Exposição da Indústria Portuguesa* (Great Exhibition of Portuguese Industry) in 1932 (Lisbon); and (iv) the opening of the *I Congresso da Indústria Portuguesa* (1st Congress of Portuguese Industry) in 1933 (Lisbon) (Callapez, 2010b). In detail, whereas the depression of 1929 (i) resulted in the recognition that national industries needed to be protected (ii), the economic recovery that followed resulted in two positive outcomes in Portugal: the Great Exhibition of Portuguese Industry (iii), and the 1st Congress of Portuguese Industry (iv) (Callapez, 2000). As stated in a Portuguese journal from the 1930s, the last two events gathered important figures from the industrial sector (O Congresso, 1933 as cited in Callapez, 2010b). From this context, the first two Portuguese plastic companies were founded, Sociedade Industrial de Produtos Eléctricos (SIPE) and Nobre & Silva. Between 1940s–1960, Portugal joined the *Marshall Plan* (1948) and entered into the *European Free Trade Association* (1959) (Callapez, 2010; Matos, 2006; Almeida, 2009; Pedroso, 2009). Thus, the Portuguese plastics industry found a favourable economic environment for its development and several plastics companies were developed during this period (Callapez, 2010). Nevertheless, and similar to what has been mentioned before (e.g. for Germany), the consumer's trust in the use of plastics needed to be conquered. To this end, plastic associations and promotional efforts were implemented by the Portuguese Government. *Grémio Nacional dos Industriais de Composição e Transformação de Matérias Plásticas,* GNICTMP (National Corporation of Plastics Materials Converters) was founded in 1957 (Callapez, 2000) and *Instituto Nacional de Investigação Industrial* (INII) (National Institute of Industrial Research) in 1959 (Almeida, 2009). From these important associations, national publications reporting the plastics production and consumption in Portugal were launched, and exhibitions promoting plastic products started to be held in Lisbon. Side by side with the effort to promote plastics, design was also paving its first steps in the renovation of the country's industrial sector.

During the 1950s, the Portuguese dictatorship regime wanted to increase the people's desire for national production. Because of this, the industries suffered serious renovation and new entities were

created with direct links to designers in an effort to include new materials, such as plastics, that would be more appealing to the modern public. With the emergence of social classes with increased economic power (including the proletariat), Portuguese industry was forced to modernise the sector and to offer products that could correspond to the new lifestyle demands. According to Graça Pedroso, furniture was definitely one of the sectors where this change towards design was most noticeable, especially because, more and more, consumers were showing interest in the acquisition of modern and functional items to equip their homes and offices (Pedroso, 2009). To this end, a union between designers and manufacturers was required (Souto, 2001), which, in the end, resulted in the beginning of design as a professional activity in Portugal (Martins, 2001; Almeida, 2009). Design associations were founded (following INII's proposal), articles about design started to appear as regular sections in national periodicals[39] and design conferences started to be held in Portugal. *Núcleo de Arte e Arquitectura Industrial,* NAAI (Art, Industrial Architecture and Industrial Design Nuclei) was launched in 1960 and for the first time, both *1ª Quinzena de Estética Industrial*[40] (1st Fortnight of Industrial Aesthetics) and the international exhibition 'Industrial Design'[41] took place in Lisbon, in 1965 (Almeida, 2009). From this context, design started to gain a high status in the country (Almeida, 2009). Along with these initiatives, the Portuguese State launched several public tenders to equip institutional spaces (hospitals, schools and banks) and leisure facilities (hotels, bars, restaurants, casinos, stores and galleries) with environments showing new and modern designs (Pedroso, 2009). In 1971, the '1st Portuguese Design Exhibition' took place in Lisbon with more than 67 designers and 46 companies (Almeida, 2009: 299) and, for the first time, the English term 'design' was heard in an official speech in Portugal (Souto, 2013).

Therefore, both Portuguese furniture design and plastic industries underwent tremendous development during this period (1960s–1970s). One of the principal leading figures of this change was definitely Daciano da Costa (Almeida, 2009; Martins, 2001). According to the historian V. Almeida, he is considered 'the father' of Portuguese Design (Almeida, 2009: 306). Daciano da Costa understood the profitable outcomes that design could offer to the industry – modern design lines produced by mass production techniques (Almeida, 2009; Martins, 2001). For these reasons, he was invited to join the Portuguese furniture company, Metalúrgica da Longra (ML) as a collaborator (Seixas, 1971; Martins,

[39] The national periodicals 'Binário: Arquitectura, Construção e Equipamento' (1958–1977) and 'Arquitectura: Arte e Construção' (1927–1984), were the main design and modern Portuguese architecture publications. In addition, 'Arquitectura: Arte e Construção' started to include a regular section specifically dedicated to design, since 1963 (Almeida, 2009: 268).

[40] At this meeting, Henri Vienot from the magazine 'Esthétique Industrielle', Giorgio Madini-Moretti from the Architecture School (Milan), Noel White from the *Council of Industrial Design*, Sergio Asti (Italian designer), Olof Gummerus from the *Finnish Society of Crafts and Design* and the Swiss Xavier Auer, attended the conference as invited speakers (Almeida, 2009: 288).

[41] In this exhibition, side by side with French, Italian and Finnish designs, furniture items designed by Daciano da Costa (Metalúrgica da Longra) and José Cruz de Carvalho (Altamira) were displayed, confirming the high quality of Portuguese industrial design production (Almeida, 2009: 288).

2001). This invitation was made by the industrial entrepreneur and director of ML, Fernando Seixas, in the early 1960s (Seixas, 1971). According to him, from that moment, Longra became the first 'design company' in Portugal (Seixas, 1971), and, during Daciano da Costa's collaborative work for ML, spaces such as offices, theatres, cinemas, hotels, shops and galleries were being equipped by his designs (Pedroso, 2009). Besides him and ML, more companies and designers were reflecting this taste for modern life and the union between design and industry. As examples, designers[42] such as José Espinho (1917–1973) worked for the firm Móveis Olaio, José Cruz de Carvalho (1930–) for Altamira and Interforma, and António Garcia (1925–) for Sousa Braga and FOC (Matos, 2002). Also, collaborations between designers was also proposed by Graça Pedroso (Pedroso, 2009). Along with Daciano da Costa, these designers adopted mass-production techniques and a modernist aesthetic view, hitherto non-existent in the country (Pedroso, 2009). However, not only original designs were being produced by some national companies. For instance, foreign models were also being copied or transformed into other objects (Almeida, 2009). According to Victor Almeida, this was being done by accessing foreign magazines or through journeys of industrial entrepreneurs to countries such as Denmark, Italy and the United States (Almeida, 2009). Olaio, Casa Jalco, Sousa Braga and Fábrica Portugal were examples of Portuguese stores offering both foreign copies and original design productions (Almeida, 2009). On the other hand, and according to Victor Almeida, this was 'decisive to the awakening of a generation to design and contemporaneity'[43]) (Almeida, 2009: 76). Nevertheless, licenses were also being established between national and international companies, as the case of ML and companies such as Hille (in England) and Airborne (in France) (Almeida, 2009; Martins, 2001).

In general, from this brief review, it is possible to conclude that plastics and other synthetic materials were being produced in Portugal. However, information concerning the importance of these new materials in the creation of novel shapes by Portuguese designers or even discussions about the entrance of PUR into this field were not found. For that reason, the following sub-sections describe the research work conducted to fulfil this gap.

2.5.1 The development of PUR industries in Portugal and PUR influence in national design

As studies focusing on the Portuguese landscape of PUR industries and PUR-based design were not found, several sources need to be included in the present research to produce the required information. These sources include the following:

[42] At this time, Portuguese universities were not offering an academic education in design. Therefore, none of these persons had a university degree in design. Instead, they were known as artists and architects, but they were also known for their will to understand design as a powerful 'tool' to improve industrial products and processes (Pedroso, 2009).

[43] Translations found in section 2.5. were made by the author of this dissertation.

(i) Study of the GNICTMP document describing the Portuguese industries active in 1973;

(ii) Online research into currently active industries producing PUR and/or PUR-based consumer goods;

(iii) Phone inquiries into currently active companies previously selected from (i) and (ii);

(iv) Survey of the online patents database of the *Instituto Nacional de Propriedade Industrial* (INPI);

(v) Survey of official documents related to public tenders to equip State buildings through the access of the national archive of *Comissão para Aquisição de Mobiliário* (CAM) from *Sistema de Informação para o Património Arquitetónico* (SIPA) at the *Instituto da Habitação e da Reabilitação Urbana* (IHRU)[44];

(vi) Collection of oral or written testimonies, after the dissemination of this research goal to former and current workers, designers, historians and firms (identified during the investigation[45]).

At the beginning of this research one of the first goals was to confirm if PUR processing industries were established in Portugal during the 1960s and 1970s. To this end, the starting point was (i) the document produced by GNICTMP in 1973, where 403 industrial firms were surveyed as active Portuguese industries (GNICTMP, 1973: 63–78). From this document, 77 firms were selected as probable producers of PUR and/or PUR-based consumer goods during the selected period. This selection was carried out by searching for specific terms within the document – fibres, foam, laminates, plastic, polyurethane, rubber, synthetic and artificial, as well as activity fields of specific companies – automotive, construction, footwear, furniture, leather-goods, mattresses and upholstery.
Curiously, the specific term 'polyurethane' was not found in this document. Even so, 77 firms were selected and two companies were added to this group after a previous (ii) online research into currently active industries.
To verify the validity of this first selection, (iii) phone inquiries and search into company databases and/or websites were carried out. From this step, only 12 companies[46] were positively confirmed as producers of PUR and/or PUR-based goods in the 1960s and 1970s. On the other hand, it could be

[44] The inclusion of this source resulted from a suggestion by João Paulo Martins (research historian), whose collaboration was crucial to this study. Martins was one of the first contacts made during this investigation and his collaboration resulted in valuable information concerning the identification of Portuguese furniture companies and the documentation of Metalúrgica da Longra's work with Daciano da Costa.
[45] In relation to the history of processing companies of PUR, personal, written or phone interviews were made with Mário Veloso (former production director) from Flexipol – Espumas Sintéticas S.A.; and with Teresa Peixoto (engineer) and Rodrigo Lencastre (commercial department), both from Monteiro Ribas. Regarding the work of furniture companies with this material, a written testimony was collected from António Pinto (former worker of Adico); and information concerning Metalúrgica da Longra was collected from email contacts to João Paulo Martins, Maria Otília Lage and Victor Almeida, as well as from a personal interview to Eduardo Afonso Dias, designer and ex. colleague of Daciano da Costa (Martins, 2001).
[46] This set includes the portuguese firms: Flexipol Espumas Sintéticas S.A.; Eurospuma; Fapobol; Têxtil Manuel Gonçalves S.A.; Monteiro Ribas; Lusoflex Espumas Rígidas E Flexíveis, S.A.; Endutex – Soc. Revestimentos Têxteis, S.A.R.L.; Molaflex; Climax Portuguesa Equip. e Mobiliario de Conforto, S.A.; Indofil - Sociedade Industrial de Filmes Plásticos, S.A.; Polipoli – Poliesteres reforçados Industriais, Lda. and Fábrica de Calçado Campeão Português, S.A.

concluded that more than 12 companies could have been working with PUR at that time since from the first set of 79 firms, six had no attributed numbers, 13 did not answer phone or email, and 33 declared bankruptcy or no phone trace was found. Because of this, the difficulty involved in the survey of former industries was acknowledged. Not only were a high number of companies not currently active, but the ones that were possible to contact reported an internal policy of not preserving documentation for more than 10 years.

Therefore, the assessment of the documentation collected from (iv–vi) started, followed by a long process of information selection.

From the study of 36 patent applications (filed between 1960–1980) found at INPI (iv), 16 firms possibly working with PUR were identified. In this set, patents related to national industrial models[47], industrial drawings, trademarks and inventions were included, following the aforementioned terms.

From the CAM archive at SIPA/IHRU (v), although more than 2000[48] file processes were available, only 200[49] were selected. This set resulted in the identification of 14 companies possibly using PUR in their furniture designs. From this archive, administrative correspondence, object descriptions, company catalogues and flyers (example shown in Fig. 2.16) and material samples were accessed, constituting rare and important documents for the discussion presented in this section.

In sum, circa 30 firms were identified from (i–v). These companies are shown in Table 2.2 that includes PUR processing industries (foams and artificial leathers), companies producing PUR-based goods (furniture, shoes and leather-goods) and furnishing stores selling these products.

[47] In this category, models of sofas and chairs were found.

[48] This starting point (2000 official processes) has already resulted from the indexing work (Excel table) previously carried out by Sofia Diniz and Margarida Elias as part of the research project PTDC/AUR-AQI/115660/2009, funded by *Fundação para a Ciência e Tecnologia* (Portugal). This project, entitled 'Móveis Modernos. A actividade da Comissão para Aquisição de Mobiliário no âmbito da Direcção-Geral dos Edifícios e Monumentos Nacionais. 1940–1980', was supervised by João Paulo Martins and aimed at studying the wide range of documents included in the public tenders for the acquisition of furniture to equip Portuguese public buildings and monuments, among other tasks.

[49] Each process showed an average of 50 pages (some more than 100 pages), which highlights the required time to assess the complete set of documents found at the archive. In this way, only 200 were selected based on the information already collected by the project PTDC/AUR-AQI/115660/2009 and its relevance to the present research.

Figure 2.16 Example of a catalogue page collected at CAM archive (SIPA/IHRU) describing the application of a 'estrutura moldada em espuma de poliuretano rígida' (polyurethane rigid foam structure) by Seel from Seldex. Description highlighted in red.

Table 2.2 Identified Portuguese companies possibly working with PUR in the 1960s and 1970s: PUR processing industries (foams, artificial leathers and soles), companies producing PUR-based furniture/leather-goods and furnishing stores.

Company / Foundation date		PUR Form / Object	Identified Clients	Source
Flexipol Espumas Sintéticas S.A. (São João da Madeira)	1964	Foams and mattresses	Metalúrgica da Longra, Olaio, Seldex, Adico and Molaflex	Phone interview with Mário Veloso (former Production Director of Flexipol); written interview with António Pinto (former worker of Adico)
Eurospuma (Espinho)	1965	Foams	Fábrica Osório Castro, Metalúrgica da Longra, and Adico	Phone call to Eurospuma (Victor Sá); phone interview with Mário Veloso; written interview with António Pinto (former worker of Adico)
Fapobol-Fábrica Portuense de Borracha, LDA (Porto)	1971	Foams and Furniture	General consumer	Phone interview with Mário Veloso and INPI
Lusoflex Espumas Rígidas E Flexíveis, S.A. (Porto)	n.f.	Foams and mattresses	n.f.	Online research
Polipoli – Poliesteres reforçados Industriais, Lda (Espinho)	1969	n.m.	n.m.	Phone call to Polipoli
Monteiro Ribas (Porto)	1937	Artificial leathers and coatings	Seldex, Metalúrgica do Levira and Ambar (furniture producers); and Laurentino C. Barbosa, Herculano Freitas Mota (stockists)	Written interview with Rodrigo Lencastre (Commercial Department of Monteiro Ribas) and INPI
Têxtil Manuel Gonçalves SA (TMG) (Vila Nova de Famalicão)	1965	Artificial leathers and coatings, leather goods and shoes	Comboios de Portugal (C.P.), Nike, MODARTE and JOP (stockists)	Phone calls to TMG (Julieta Magalhães) and INPI
Endutex – Soc. Revestimentos Têxteis (Vilarinho)	1970	Artificial leathers and coatings	n.f.	Online research

Indofil - Sociedade Industrial de Filmes Plásticos, S.A. (Castelo da Maia)	1970s (?)	n.m.	n.m.	Phone calls to Indofil (Manuela Pinheiro) and INPI
Fábrica de Calçado Campeão Português, S.A. (Guimarães)	1955	Shoes	General consumer	Online research and INPI
Molaflex (S. João da Madeira)	1951	Mattresses	n.m.	Phone interviews with Mário Veloso and CAM archive (SIPA/IHRU)
Climax Portuguesa Equip. e Mobiliario de Conforto, S.A. (Sintra)	1969	Mattresses	n.f.	Online research; CAM archive (SIPA/IHRU)
Metalúrgica da Longra, Limitada (Longra)	1920	Furniture	Portuguese State and general consumer	INPI and CAM archives (SIPA/IHRU)
Seldex-Sociedade de Equipamento de Escritório, S.A. (Queluz de Baixo)	1969	Furniture	Portuguese State and general consumer	INPI and CAM archives (SIPA/IHRU)
FOC Fábrica Jerónimo Osório de Castro (Mafra)	1930	Furniture	Portuguese State and general consumer	Phone interview with Mário Veloso; CAM archive (SIPA/IHRU)
Handy Portuguesa, Lda. (Aveiro)	1970s (?)	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
Fábrica Portugal (Lisboa)	b. 1890	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
Ádico (Avanca)	1920	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
Janeves, Móveis Metálicos para Escritório e Indústria (Avanca)	1930	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)

Raul Azevedo, Lda. Móveis, Estofos, Decorações, Adornos (Porto)	n.f.	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
Sano-Técnica, Lda. (Lisboa)	1938	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
José Olaio e C.ª (FILHO) (Lisboa and Porto)	1886	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
Lusodex Lda. (Lisboa)	n.f.	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
J. Sousa Braga - Móveis Decorações (Lisbon)	n.f.	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
Móveis Baía (factory in Barreiro and store in Lisbon and Barreiro)	n.f.	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
Companhia dos Grandes Armazéns Alcobia, S.A.R.L. (Lisbon)	1914	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)
Sularte-Sociedade Industrial de Estofos, Lda. (Barreiro)	n.f.	Furniture	General consumer	INPI
João Vasco Félix da Costa d'Alcântara (Lisboa)	n.f.	Furniture	General consumer	INPI
Porfírio Moreira da Silva (Lisboa)	n.f.	Furniture	General consumer	INPI
Joachim Mitnitzky, Decorações Lda. (Lisbon)	1960s (?)	Furniture	Portuguese State and general consumer	CAM archive (SIPA/IHRU)

Nacital-Companhia Nacional de Com. e Metalúrgica, S.A. (Lisboa)	1957	Furniture	General consumer	INPI
Artur Gomes Moreira (Maia)	n.f.	Furniture	General consumer	INPI
José Ribeiro & Guerra (Águeda)	n.f.	Artificial leathers	Adico	Written interview with António Pinto (former worker of Adico)

n.m. not mentioned; n.f. not found; b. before; (?) probable date

Besides this information, assessing CAM's archive allowed the identification of prior or more traditional art materials used for padding (furniture and mattresses) and frame construction, as well as contemporary replacements of PUR foams. In this case, while PUR flexible foams (for mattresses and pillows) were commonly mentioned as substitutes of 'folhelho' (husks of corn or other seed), 'sumauma' (Kapok) (DGEMN:CAM-0005/9, SIPA TXT.07001362) and 'corticite' (cork) (DGEMN:CAM-0018/9, SIPA TXT.07009577), PUR rigid foams (moulded) were mentioned as replacements for wood and metal frames (DGEMN:CAM-0424/02, SIPA TXT.07269680). Latex and rubber foams were considered similar materials to PUR flexible foams.

To summarise the industrial terms and brands mostly used for the description of padding and cover materials, Table 2.3 was designed. From this table, it may be concluded that modern and synthetic materials were well-known to Portuguese companies as well as frequently considered to produce chairs, sofas and mattresses. In detail, 'calf plástico' (plastic calf), *Ultraflex* (trademark), 'pergamoide' (pegamoide), napa and *Sky* or *Skay* (trademarks) were commonly found in the description of artificial leathers (used as covers); and 'espuma de látex' (latex foam), 'espuma de borracha' (rubber foam), 'espuma de poliuretano' (PUR foam), *Moltopren* (trademark), *Poliflex* (trademark) and *Dunlopillo* (trademark), commonly stated for the description of padding.

Although Metalúrgica da Longra (ML) and Fábrica Osório Castro (FOC) only described the use of latex and rubber foams (see Table 2.3), further infrared analysis of two case studies from the MUDE collection confirmed the presence of PUR foams. The reasons for this incorrect material attribution (in the company documents) might be: the novel (in the 1970s) introduction of this material in Portuguese companies; the similar appearance between latex and PUR foams; and finally, the previous and common use of latex foams. Consequently, the identification of materials in museum collections

through labels or industrial indications should be followed by a careful assessment of the information and if possible, confirmed by material characterisation.

Table 2.3 Examples of industrial terms and brands related to the production of upholstered furniture and mattresses (padding and covers), commonly found in documents from the CAM archive at SIPA/IHRU

ID CODE / Date	Company	Industrial Term/Brands Identification		
		Term	**SIPA TXT Nº**	**Document Type**
PT DGEMN:CAM-0005/9 1971	Fábrica Jerónimo Osório de Castro (Herdeiros), Lda.	Calf plástico (cover)	07001360; 07001362	Textual
		Espuma de látex (padding) *Ultraflex* (cover)	07001391; 07001392; 07001404	FOC catalogue
		Casco de poliuretano endurecido (structural material)	07001427; 07001430	Textual/Table
	Sano-Técnica, Lda.	Espuma de borracha (padding) Calf plástico (cover)	07001438	Textual/Table
PT DGEMN:CAM-0018/11 1970	Metalúrgica da Longra, Lda.	Pergamoide (cover) Espuma de borracha (padding)	07009587	Metalúrgica da Longra catalogue
PT DGEMN:CAM-0018/12 1971	Companhia dos Grandes Armazéns Alcobia, SARL	Calf plástico (cover)	07009675; 07009676	Textual/Table
PT DGEMN:CAM-0071/13 1970	Raul Azevedo, Lda.	Espuma (padding) Calf plástico (cover)	07049657	Textual/Table
PT DGEMN:CAM-0267/02 1974	Handy Portuguesa, Lda.	Casco de poliuretano endurecido (structural material) Napa (cover) Espuma de borracha (padding)	07179209	Textual/Table

PT DGEMN:CAM-0418/18 1974	J. Sousa Braga - Móveis Decorações	*Sky* (cover)	07265307	Material sample
		Espuma de borracha (padding)	07265311	Textual
		Colchão de molas *Molaflex* (padding)	07265312	
		Colchão de espuma de borracha (padding)		
	Sano-Técnica, Lda.	Espuma de poliuretano (padding)	07265315	
	Fábrica Jerónimo Osório de Castro (Herdeiros), Lda.	Colchões *Climax* (padding)	07265326	Textual/Table
	José Olaio e C.ª (FILHO) Olaio	Colchão de molas *Molaflex* (padding)	07265330	Textual
PT DGEMN:CAM-0423/5 1972	Fábrica Jerónimo Osório de Castro (Herdeiros), Lda.	Casco de poliuretano (structural material)	07269323	Textual/Table
		Napa (cover)		
		Espuma *POLIFLEX* (padding)	07269324	
	José Olaio e C.ª (FILHO) Olaio	Espuma *MOLTOPREN* (padding)	07269331	
		Skay (cover)		
	Móveis Baía	Espuma (padding)	07269333	
		Napa (cover)		
PT DGEMN:CAM-0424/1 1971	Seldex-Sociedade de Equipamento de Escritório, Lda.	Espuma de borracha (padding)	07269556; 07269561	Seldex catalogue
		Napa (cover)		
		Estrutura moldada em espuma de poliuretano rígida (structural material)	07269562	
	Metalúrgica da Longra, Lda.	Estofo de espuma de látex (padding)	07269577; 07269591	Metalúrgica da Longra catalogue
		Napa (cover)		

PT DGEMN:CAM-0424/2 n.d.	Ádico	Pergamoide lavável (cover) Espuma de borracha (padding)	07269665; 07269666; 07269672	Ádico catalogue
	Fábrica Jerónimo Osório de Castro (Herdeiros), Lda.	Estrutura de poliuretano (structural material) Estofo de espuma de látex (padding) Revestimento com *Ultraflex*	07269680	FOC catalogue
	Janeves, Móveis Metálicos para Escritório e Indústria	Espuma de poliéster (padding) Napa (cover)	07269714; 07269716	Janeves catalogue
PT DGEMN:CAM-0443/6 1972	Sano-Técnica, Lda.	Espuma de latex (padding)	07284827	Textual
	Fábrica Jerónimo Osório de Castro (Herdeiros), Lda.	Espuma de borracha *Dunlopillo* (padding)	07284840	Textual/Table

n.d. no date

From the trademarks shown in Table 2.3, *Moltopren, Molaflex* and *Poliflex* could be brands of PUR products. *Moltopren* was already identified in section 2.3 as a trademark from Bayer, and the remaining brands are discussed later in this section. Overall, valuable and crucial information was collected from INPI's patent database and CAM's archive.

On the other hand, the reasons that led industrialists and designers to choose PUR over other options continued to be lacking, as well as references discussing the entrance of this industry in Portugal. To this end, the collection of personal testimonies (vi) has been decisive. In addition, further documentation was produced, concerning the following topics:

a) Establishment of PUR processing industries in the country;
b) Advantages of using PUR in fashion and product design items.

Regarding the first topic (a), two important testimonies were collected from Mário Veloso (Flexipol) and Rodrigo Lencastre[50] (Monteiro Ribas). These testimonies enabled the production of more information about the foundation of two of the most important PUR processing industries in the

[50] According to Rodrigo Lencastre, the answers in his written testimony assembled testimonies from different workers from Monteiro Ribas. Nevertheless, their names were not provided, and so this information is solely attributed to R. Lencastre.

country in this period – Flexipol, as a producer of PUR foams; and Monteiro Ribas, as a producer of PUR-based leathers.

According to M. Veloso, Flexipol was founded in 1964 (São João da Madeira) by Viana da Rocha and Sampaio Peixoto (engineers from Shell in the Netherlands) to fill a material necessity by the nearby company, Molaflex (M. Veloso, phone interview, May 31, 2013). Molaflex, initially dedicated to the production of chairs for trains, decided to expand its service to spring mattress (Cardoso, 2012 as cited in Braz, 2015: 1). Consequently, being Shell, a manufacturer of PUR raw materials and Molaflex, a processing unit of mattresses, the profitable business raised by the two companies was quickly recognised (M. Veloso, phone interview, May 31, 2013). As a result, Flexipol was born and Molaflex started to produce PUR foam mattresses[51]. According to M. Veloso, the raw materials and the technical equipment required for the foundation of Flexipol in Portugal were not entirely provided by Shell. Bayer and the later Portuguese company, Isopor – Companhia Portuguesa de Isocianatos, Lda[52] (Estarreja) – were also suppliers of Flexipol, along with Cannon Viking (Manchester, UK), which supplied the machinery. Regarding possible competitors, M. Veloso mentioned the parallel existence in this period of Eurospuma (Espinho, 1965–) and Fapobol (Porto, 1971–). This highlights the probable success of PUR industries in Portugal as several companies appeared simultaneously in the country during this time.

Concerning the company Monteiro Ribas, the interview focused on the national production of artificial leathers and coatings. According to R. Lencastre, although this company started in 1937 with Josué Monteiro and Almiro Monteiro[53] as a tannery industry, only in 1966 were new markets explored (R. Lencastre, written interview, June 20, 2013). This aim was truly achieved with the entrance of the engineer Durval Carteado Mena. Along with products made of rubber and plastic, in 1966 Monteiro Ribas started the production of artificial leathers to fulfil the demand for upholstery, leather goods and footwear (R. Lencastre, written interview, June 20, 2013). This production started with PVC but PUR-based products were introduced in the early 1970s. Similar to the previous case, both raw materials and machinery came from foreign countries. Bayer and Stahl (The Netherlands) were mentioned as the suppliers of PUR raw materials as well as responsible for the entrance of PUR in the company and Germany as the country from which machinery was acquired (R. Lencastre, written interview, June 20,

[51] Molaflex is the company name but also the trade name of PUR foams. Regarding other Portuguese companies producing mattresses, *Poliflex* was identified during this research as a trademark of both Molaflex-Colchões, S.A. since 1965 and Lusoflex – Espumas Rígidas e Flexíveis, S.A., since 1972 (national trademark patent nº 130142 and nº 176204, INPI).

[52] According to the Dow website, Isopor was founded from the commercial interest of Química de Portugal, E. P. - Quimigal (Portugal) and Upjohn (USA) in 1978, becoming Dow Portugal in 1989 (The Dow Chemical Company, 2016).

[53] According to R. Lencastre, these two workers were trained abroad in tannery processes in France and England, respectively.

2013). Regarding possible competitors, once more, Monteiro Ribas was not the only industry serving Portugal with PUR artificial leathers. According to R. Lencastre, the company Têxtil Manuel Gonçalves was the first firm to introduce these leathers at a national level and, in this way, became one of the main competitors of Monteiro Ribas (R. Lencastre, written interview, June 20, 2013).

Concerning the advantages of using PUR in fashion and product design (a), three testimonies were collected from António Pinto (former worker at Adico), Teresa Peixoto (current engineer at Monteiro Ribas) and Eduardo Afonso Dias (designer and ex. colleague of Daciano da Costa).
According to A. Pinto (Adico), before the introduction of PUR flexible foams in furniture, the padding process involved the application of three layers: one of palm leaves (acquired as string bales, which required specific machines for handling); a second of cotton fibres (acquired as pressed rolls); and finally, a crude fabric (A. Pinto, written interview, May 14, 2014). Therefore, the technical and practical advantages brought by PUR foams can be imagined as highly appreciated by industrialists, mostly, because only one layer would then be necessary.

> 'The use of polyurethane foam is more practical, more hygienic and easier to use as it replaces at least two materials and two tasks. It has reduced the hand labour required for these operations' (A. Pinto, written interview, May 14, 2014).

Moreover, Pinto mentioned the profit use of TPU films and coatings for the production of artificial leathers. In his words, this leather 'is easier to work because it is not hard' (A. Pinto, written interview, May 14, 2014). Regarding PUR foams, he stated that their use 'allowed the production of forms with increased comfort', which enabled the creation of new and attractive shapes in furniture (A. Pinto, written interview, May 14, 2014).
In agreement, Teresa Peixoto added further advantages to the use of PUR-based leathers: better resemblance to natural leather than PVC and enhanced resistance to alcohol (T. Peixoto, personal communication, October 31, 2013). Their profit use over PVC was also stated by T. Peixoto in relation to environment legislations that regulate the production and use of chemical substances (e.g. REACH). Since only *Clear to Wear* colorants are allowed, PUR formulations were mentioned as better options than PVC due to their low viscosity and better dispersion qualities (e.g. of dyes).
The testimony of Eduardo Afonso Dias (1938–) allowed the perspective of a designer who has worked side by side with industrial companies to be added. According to his testimony, design in Portugal was still making its first steps during the 1960s and 1970s (E. A. Dias, personal communication, January 20, 2014). In general, industrial companies were not inviting designers to create new objects and the common tendency was to copy foreign designs through industrial espionage or established partnerships. Although E. A. Dias mentioned that he had worked with more than 70 companies

throughout his professional life (mostly, since the 1970s), he also explained that this achievement was only possible due to his own initiative and perseverance, but mostly was based on his own search for markets, material possibilities and shapes[54].

Regarding the use of plastics, Dias mentioned that he looked at this material as a chance to create new forms and to turn innovation economically viable. According to him, plastics could be used to promote quality in design but should fulfil a particular need in the market. Concerning PUR, Eduardo Afonso Dias confessed that this was not a common material in his designs. Nevertheless, he described its use in chairs and sofas (as flexible foams) due to its capacity to offer different foam densities that could be used to create different supports and comfort. He has also mentioned the use of artificial leathers based on PUR as profitable choices for design. According to his testimony, these leathers show an appearance comparable to natural leather, are cheaper and offer the possibility of being breathable (E. A. Dias, personal communication, January 20, 2014). During his work for ML, he had contact with some of these materials, met Daciano da Costa and learned more about design processes. Other crucial information provided by E. A. Dias was the professional relationship of ML with both Portuguese and international renowned firms. As examples, he mentioned Eurospuma, Flexipol and Monteiro Ribas as Portuguese companies with which ML was working at that time, and Hille (England) and Airborne (France) as examples of international firms that were part of ML partnerships. As stated in the interview, ML was probably acquiring PUR frames from foreign companies (e.g., Hille), PUR flexible foams from Eurospuma and Flexipol, and PUR-based artificial leathers from Monteiro Ribas (E. A. Dias, personal communication, January 20, 2014). According to Deodato Martins (previous worker of ML and collaborator of Daciano da Costa), this closer contact with other companies may have allowed ML to get in touch with modern design practices and processes as well as with new materials and production techniques (Martins, 2008 as cited in Almeida, 2009: 277).

2.5.2 Documentation of Metalúrgica da Longra's work with PUR in the 1960s and 1970s

Given the relevance of the found information concerning the specific work of Metalúrgica da Longra (ML) with PUR, this company is studied in detail[55]. Regarding this subject, the information previously discussed is here complemented with additional documentation found at SIPA/IHRU and with further oral and written testimonies collected during this research.

[54] Once more, and as supported by E. A. Dias, ML's work with Daciano da Costa can be considered a unique case of a firm uniting design and industry methodologies in Portugal during the 1960s and 1970s.

[55] It is important to emphasise that besides ML, other furniture companies were identified as singular cases of Portuguese firms innovating in design and working with PUR (e.g. FOC). However, due to the scarcity of testimonies and publications concerning their history, it was not possible to produce further documentation about their work with this material.

From the archive *Daciano Monteiro da Costa* (DMC) at SIPA/IHRU, more documents from the period of the designer's work at ML were found — among them, it was possible to access informative bulletins, technical drawings, company internal correspondence and flyers. Contrary to the information previously discussed (section 2.5.1), these documents allowed the confirmation that the specific term 'polyurethane' was being commonly used by the company to describe padding and leather-like products (Table 2.4). Besides, two trade names of high quality PUR leather products were identified: *Ventil* (English product) and *Lezíria* (German product). These products were described as true replacements for natural leathers and were highly used by the French company, Airborne.

Table 2.4 Relevant information concerning the use of PUR by Metalúrgica da Longra collected from informative documents found at the DMC archive (DMC 22 47 3, SIPA/IHRU)

Date	Document Subject	Industrial Term	Additional description
January 1972	Production and sale of the *Orchidée* by Airborne	'Napa de poliuretano *Ventil*'	English manufacturer
		'Espuma flexível de poliuretano'	-
February 1972	Sale of the *RDI – ARCA – FSIA* armchair by Robin Day, produced by Hille	'Espuma flexível de poliuretano'	-
April 1972	Production of Airborne models	'Napa de poliuretano *Lezíria*'	German manufacturer Superior quality than *Ventil,* pleasant to touch, resistant to T variations, dirt repellent, colour stable, resistant to use and breathable

From the observation of chair technical drawings designed by Daciano da Costa, it was possible to observe that the visual representation of PUR foams followed the same industrial standards as the ones shown in section 2.2. For example, dotted areas were commonly used to represent foamed materials (Fig. 2.17) and different foam densities were represented by areas with more or less dots (Fig. 2.18). Higher densities were used for the lumbar and leg bending regions, whereas lower densities were selected for the seating area. Therefore, Daciano da Costa was taking advantage of the wide offering of PUR density grades and was aware of graphical representations of materials.

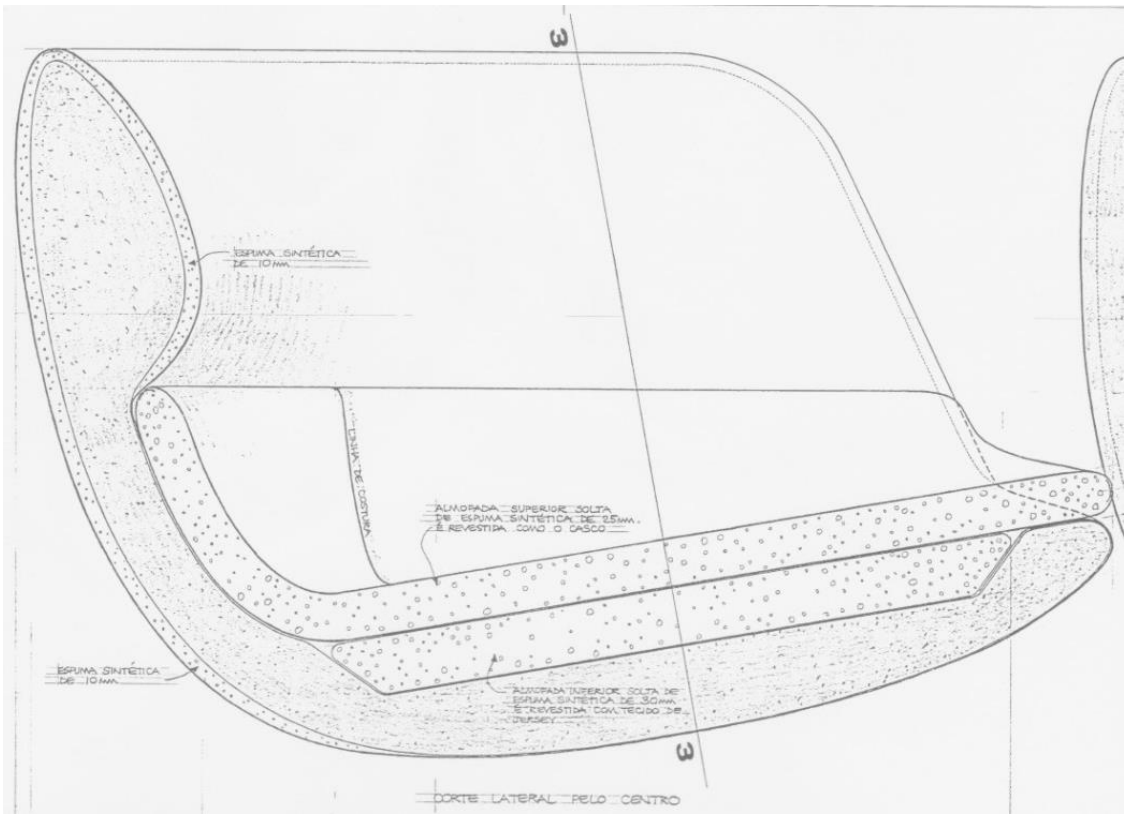


Figure 2.17 Detail of the *polyurethane chair 'C'* technical drawing, 1970, by Metalúrgica da Longra, showing dotted areas to represent foamed materials (PT DMC DES.04230, SIPA/IHRU).

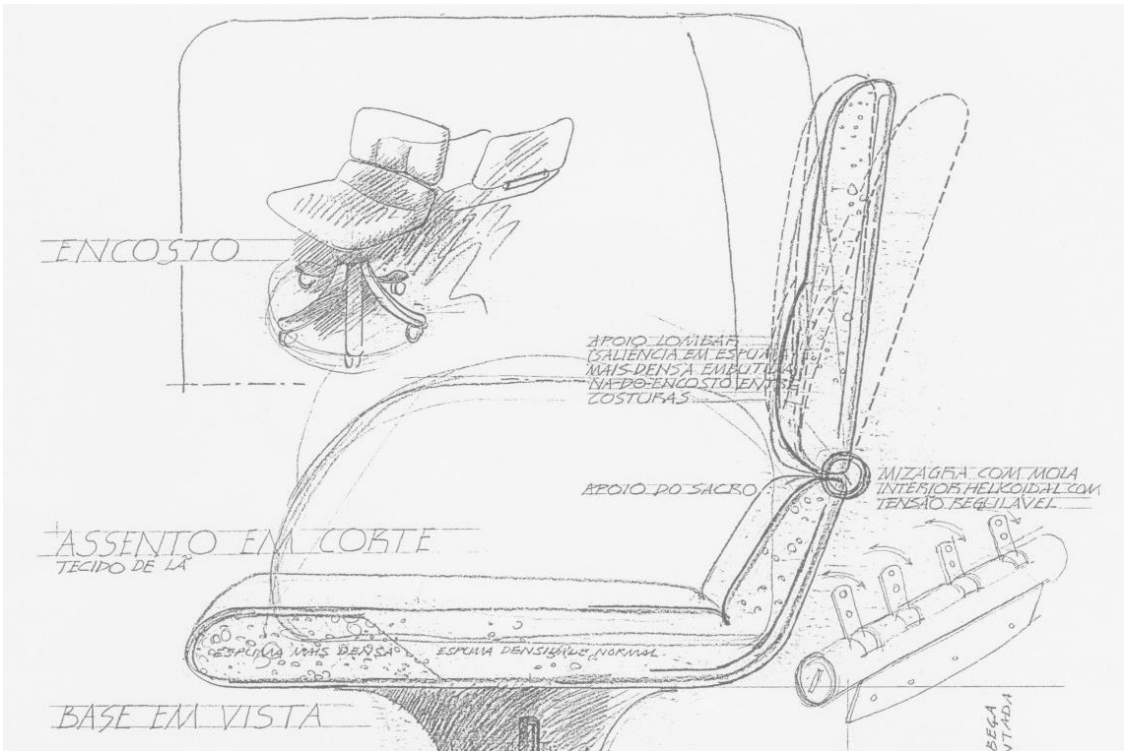


Figure 2.18 Detail of a working chair technical drawing, 1986, by Metalúrgica da Longra, describing the use of different PUR foam densities (PT DMC DES.04296, SIPA/IHRU).

Company documents related to the planning of a specific PUR chair made of moulded PUR rigid foams were also found during this investigation. These documents included technical drawings and correspondence letters between Daciano da Costa and ML (1970–1972) and have confirmed ML's wish to implement new technologies in its firm. However, according to J. P. Martins (Martins, 2001: 264) and oral testimonies[56] collected during the present research, this chair did not enter into serial production. Still, one plausible reason for this decision (not to produce the PUR chair) can be suggested. As stated by P. Sparke, new plastic materials (such as PUR rigid foams) involve high costs in production, especially when mould production is required (Sparke, 1988). Therefore, the use of moulds made of synthetic materials was mostly channelled to high-scale projects (Sparke, 1988). This was also mentioned by E. A. Dias during his interview (E. A. Dias, personal communication, January 20, 2014). According to his testimony, as most of his works were intended to value the individuality of design and the production of furniture that should stand out for its singular creation; the financial investment required for the production of a mould was not sufficiently sustainable to support the production of a short number of items. Thus, the use of frames made of moulded PUR rigid foams was limited or purchased from subcontracted companies. Still, PUR can be definitely identified as an important material for the company – not only PUR flexible foams and PUR-based leathers were being used in ML's designs, but PUR rigid foam frames were part of its future plans.

Concerning ML's partnership with Airborne, further information was collected. As known, the French company has been particularly acknowledged for its work with Olivier Mourgue (and the popular *Djinn* series); and, according to several authors, ML and Airborne had established a partnership during the 1960s (Martins, 2001; Almeida, 2009). However, the possible role of Airborne in the introduction of PUR in ML's designs has not been discussed, even though Airborne had commonly worked with PUR during this period. For that reason, this hypothesis was posed.

From the CAM archive at SIPA/IHRU, flyers of ML promoting its partnership with Airborne (Fig. 2.19) were found. From these documents, photographs of rooms equipped with Airborne designs as well as texts describing the high quality of its products were accessed. Nevertheless, the specific term 'polyurethane' was not found.

[56] Although further testimonies were collected from John David Bear and Eduardo Afonso Dias (ex. colleagues of Daciano da Costa in his atelier) and Mário Brilhante (former worker of ML and colleague of Daciano da Costa), the reasons behind this decision have not been identified. John David Bear explained that he had been solely involved in the drawing phase, Mário Brilhante that he had been exclusively dedicated to traditional materials, and Eduardo Afonso Dias that he did not participate in this project (J. D. Bear, phone interview, 2013; M. Brilhante, phone interview, 2014; E. A. Dias, personal communication, January 20, 2014).

Figure 2.19 Room equipped with Airborne designs from the flyer 'Metalúrgica da Longra, Lda. airborne, licence francesa' (PT DGEMN:CAM-0443/8; SIPA TXT. 07284914).

In an article published in the magazine 'Arquitectura', M. João Leal describes the opening of the exhibition 'Longra-Airborne furniture' in Lisbon, in 1967, planned by ML to promote this partnership (Leal, 1967: 266–267). Even though the author describes the *Joker* and *Djinn* series (using PUR) (Fig. 2.20) as bold design ideas of Airborne (Leal, 1967), once more, the term polyurethane was not found. For that reason, additional sources were added to document the relationship established between the two companies and to confirm if this partnership did influence ML to work with PUR. According to E. A. Dias, the leading figure of this partnership was Fernando Seixas (E. A. Dias, personal communication, January 20, 2014). As he says in the interview, during F. Seixas's travels to other countries with the goal to expand ML's market, he contacted the French company Airborne and established the license. From this statement and with the previous knowledge that ML was selling Airborne's designs, several questions were posed. Were these products produced by Airborne and brought to Portugal? Or, were they entirely produced by national companies? Did Airborne influence ML to innovate its design and industrial production?

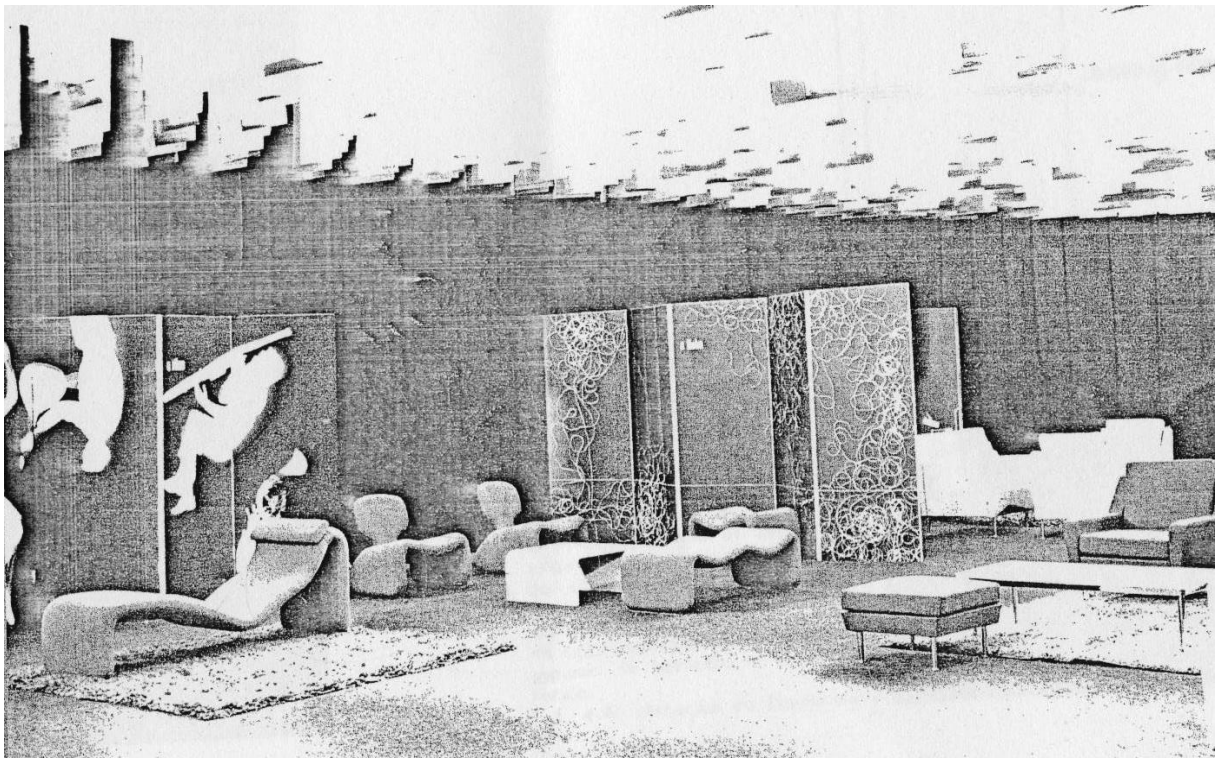


Figure 2.20 View of the Airborne exhibition produced by Daciano da Costa, Tomás de Figueiredo and Eduardo Afonso Dias from Metalúrgica da Longra, in Lisbon, 1967. Detail view of the *Djinn* series (Leal, 1967: 267).

Regarding this subject, the testimonies of José Alves Pereira[57] (former engineer at ML) and Maria Otília Lage added important information. According to J. A. Pereira, ML was producing the licensed Airborne designs (J. P. Martins, personal communication, June 25, 2012). The engineer mentioned the *Storm* chair as a result of that license. In this case, the PUR foams used to produce the *Storm* chair were supplied by a national company (J. P. Martins, personal communication, June 25, 2012). In agreement, Maria Otília Lage mentioned that the import of foreign elements to be assembled in Portugal was not a common practice in ML (M. O. Lage, personal communication, June 21, 2012). Consequently, the national production of Airborne designs might have been confirmed as well as the combination of industrial services provided by both ML and subcontracted national companies. In addition, M. O. Lage stated that the professional relationship between ML and Airborne also resulted in skilled labour training (M. O. Lage, personal communication, June 21, 2012), which highlights this partnership as a licensing of designs, but also as a transfer vehicle of industrial and material knowledge. This possibility is also supported in Victor Almeida's PhD dissertation through the testimonies of Deodato Martins (Martins, 2008 as cited in Almeida, 2009: 277) and Fernando Pinto (Pinto, 2008 as cited in Almeida, 2009: 277), both previous workers of ML. Although it is not possible to confirm Airborne as the primary

[57] This testimony was kindly collected by João Paulo Martins.

source responsible for the introduction of PUR in ML's designs, it is possible to confirm its influence in ML exploration of different materials and design shapes of which PUR was part.

2.6. Conclusions

The main goal of this chapter is to contribute to a more complete biography of PUR during the time-frame of the present research. It was aimed at documenting the relationships between PUR and both the manufacture and processing industries, and also at identifying the key reasons for the selection of PUR over other materials. To achieve this goal, the present research followed inter- and multidisciplinary approaches, gathering information from both primary and secondary sources. PUR patents published between 1960 and 1981 were surveyed; marketing initiatives by Bayer and its work with international renowned designers were studied, and the work of two important Italian companies with PUR was documented. Finally, this chapter also looked at the foundation of PUR processing industries in Portugal and the work of Portuguese designers with this material. Liaisons between the collected information and iconic PUR-based objects from the MUDE collection have been established. The study of industrial patents enabled a worldwide perspective of PUR industry in the 1960s and 1970s, a higher knowledge about the construction of PUR-based objects, and the identification of inventors and material achievements. These patents stood out as powerful sources for the writing of a history of PUR industry and for the study of PUR application in product design and ready to wear fashion. The knowledge about the objects' construction, namely the application of different PUR foam densities (in the same object), the unexpected presence of PUR foams inside rigid plastic structures, and the use of blended formulations (with TPU) in top coatings, added valuable information to the conservation field as a more accurate identification of materials and condition assessment of an object has been provided.

Also, the central reasons for the selection of PUR over other options have been identified. Among them light weight, strength, economic manufacture, and the possibility to produce unusual designs following mass techniques have been mentioned for PUR foams. Lighter weight and elastic fabrics, as well as the production of low denier yarns showing good dye ability and resistance to perspiration have been mentioned for PUR elastic fibres. Finally, natural appearance and feel, desirable drapeability and vapour permeability for PUR-base leathers.

Regarding the research work on Bayer, this study offered a new insight into Bayer's role in the history of PUR design and consumer acceptance of plastics. More than Bayer's role in the breakthrough of PUR chemistry, this study produces documentation regarding Bayer's promotional efforts for PUR

polymers. It was possible to conclude that Bayer strategically looked for renowned designers as key figures for the promotion of its recent material novelties and created unparalleled 'living' programmes (entitled *Visiona*) from the unique characteristics of PUR foams, fibres and leathers. As Bayer showed the talent to benefit from PUR potential in the production of outstanding furniture design, regular articles in both scientific and weekly newspapers started to appear in Germany describing the triumph of PUR.

Concerning the work of the Italian companies, Gufram and Poltronova, the worldwide appreciation of their successful and unique work with PUR has also been documented. Information regarding the designers aesthetic and material experience with PUR has been collected from personal testimonies and interviews, with workers from both companies. Gufram was created with the exclusive intention of working with this versatile polymer and the company's main goal was to invite designers to experiment with the material. Poltronova, on the other hand, was not focused on working exclusively with this material but with the aim of bringing new forms and technologies to people's homes. Still, polyurethane was selected and used by the two companies to produce bold design ideas, and none of the interviewees mentioned any other polymer that could have been used instead of the PUR foam.

In the Portuguese context, this chapter contributes to fulfilling the total void of knowledge about the history of Portuguese PUR industries and the work of Portuguese designers with this material. From this research, circa 30 firms have been identified as active in Portugal during the 1960s and 1970s, including PUR processing industries, companies producing PUR-based goods (furniture, shoes and leather-goods) and furnishing stores selling these products. This way, and unlike the common notion of an industrially backward Portugal, this research shows that Portugal had a place on the PUR map.

Overall, PUR has completely changed the world of fashion and product design during the 1960s and 1970s by offering comfortable, unusual, stylish and luxury objects. There is no doubt that PUR combined freedom of design and functionality, brought novel design possibilities, shapes and better comfort to the user. It also enabled designers to conduct experiments with the material, pushing their creativity to the limit.

CHAPTER 3

DEGRADATION STUDIES FOR PUR-BASED CASE STUDIES FROM THE MUDE COLLECTION

Part of the content of this chapter has already been published:

França de Sá, S., Ferreira, J. L., Pombo Cardoso, I., Macedo, R., Ramos, A. M. 2017. Shedding new light on polyurethane degradation: Assessing foams condition in design objects. *Polymer Degradation and Stability*. DOI: 10.1016/j.polymdegradstab.2017.08.028.

3.1. Preamble

The main goal of this chapter is to assess the condition of PUR from selected case studies from the MUDE collection. As discussed before, the large set of PUR-based objects in the collection, along with the short lifespan of this synthetic polymer made this study a priority. In MUDE, although the presence of PUR in the collection is recognised by the museum staff, the wide class of PUR is not entirely acknowledged, the use of this material in areas such as product design and fashion is not fully understood, the knowledge about the selected objects' creative processes is still insufficient, and the materials are not characterised. Consequently, and for the museum, this study is the starting point of a deeper research work about PUR in this collection.

The main criteria for object selection consisted of provenance (nationality of design company/author), PUR form and type, as well as condition grade. The selection intended to cover national and international case studies, the wide range of PUR forms (foams, coatings and fibres) and types (ether- and ester-based), and different condition grades (ranging from fair to unacceptable).[58] Since flexible foams (conventional, moulded and quasi collapse), films, coatings and fibres are shown by the case studies, model samples were necessarily produced for comparative reasons (serving as unaged references to be submitted to ageing experiments). The models produced aimed at following typical PUR formulations (with high commercial importance) and covering the wide variety of PURs found in the collection. In this way, it would be possible to extend the usefulness of the data obtained to different case studies and museums. Closer formulations with the historical objects were confirmed by IR and Raman spectroscopies, increasing the validation of their use as model samples.

As discussed in Chapter 1, although the deterioration of PUR has been widely investigated, none of these studies has focused on the possible deterioration of hydrogen-bonding interactions within PUR segregated structure as a consequence of natural ageing processes. Since polyurethanes 'are strongly self-associated through intermolecular hydrogen bonding' (Coleman *et al.*, 1988: 60), and these bonds play a significant role in the design and preservation of the physical and chemical properties of the material, this chapter looks at the deterioration of polyurethanes with a special focus on these bonds. The methodology proposed in the present chapter – to follow H-bonds during natural ageing processes through molecular and micro visual approaches – contributes to the current knowledge of PUR deterioration, with its supramolecular structure being proven as a key aspect for this understanding. Moreover, this chapter discusses different fluorescence behaviours (based on images acquired under the microscope) of unaged models and aged PUR historical objects.

[58] In this paper, the scales used for the definition of condition grades are divided into good, fair, poor and unacceptable, as proposed in the survey form designed by the European *POPART* Project (Lavédrine *et al.*, 2012a: 297).

For the characterisation of PUR[59], optical microscopy (under darkfield, polarised light and UV light) and IR spectroscopy (transmission mode) have been used to assess the visual aspects of polyurethane as well as the deterioration at the molecular level. Raman spectroscopy was also applied but due to the limitations of the technique when analysing yellowed and/or highly degraded foams, it was not possible to acquire spectra with good spectral resolution in all cases. Still, the technique proved to be highly efficient in the characterisation of good and fair conditions and therefore, the results are shown in Appendix V[60]. The results from the assessment of the historical objects' condition were compared with those from the assessment of two ageing experiments carried out for each model. The models were exposed to both artificial (UV-Vis radiation, λ>300 nm) and natural (outdoor) ageing conditions in order to simulate ageing pathways as found in objects from the museum collection, and to validate the attributed condition grade. Although the outdoor conditions are not controlled, this ageing experiment enabled studying the effect of fluctuating weather conditions. From this, some similar ageing courses as shown by the selected case studies were produced and a visual and molecular pathway for PUR deterioration is suggested, especially for ether-based PUR flexible foams (slabstock and cold-moulded), where more case studies were assessed. A hypothesis for the deterioration of H-bonds is also proposed.

3.2. Assessing degradation on PUR historical objects

Methodology

The MUDE collection holds a high number of objects (c. 20%) showing PUR elements with different PUR forms, types and condition grades. From this collection, 24[61] case studies have been selected for thorough assessment[62]. The 24 objects have been divided into 3 main groups: flexible foams (17), TPU coatings/films (5), and TPU fibres (2). Within foams, ether- (15) and ester-based (2) PURs have been identified by IR spectroscopy; and within ether-based foams, slabstock (10) and moulded (5) processes have been found. The whole set of objects showing TPU coatings/films has been identified as ester-

[59] Although the whole set of case studies is composed of materials other than PUR, this thesis aimed at focusing its entire attention on PUR.
[60] The powerful application of Raman spectroscopy in the characterisation of early stages of ageing is discussed in-depth in Chapter 4 for the assessment of a dark ageing experiment.
[61] Although more case studies from the MUDE collection could have been selected, only 24 have been characterised due to material accessibility for sampling. Contrary to TPU coatings/films, PUR foams are typically found in the interior of furniture objects, and TPU fibres are generally blended with other fibres as a minor percentage. For that reason, the access to these materials is limited or impossible (without causing damages to the object). To avoid the collection of samples from objects which did not show any kind of opening (e.g. zippers), deterioration or damages (e.g. tears or physical abrasion), these objects were left aside, since others were easily accessed.
[62] Additional information on the case studies can be found in Appendix III.

based (by IR spectroscopy), whereas the two cases comprising TPU fibres have been confirmed as ether-based. Overall, the large diversity of PUR polymers in the collection has been proved, resulting in the assessment of 5 distinctive PUR classes (i–v), described as follows:

(i) Ether-based PUR slabstock foams;
(ii) Ether-based PUR cold-moulded foams;
(iii) Ester-based PUR slabstock foams;
(iv) Ester-based TPU films/coatings;
(v) Ether-based TPU fibres.

Three independent micro samples were collected per object, and/or per independent degraded area in the same object.

The systematic assessment of the case studies was carried out by IR spectroscopy (transmission mode) and optical microscopy (under Vis and UV light) in micro samples (see Appendix I). This approach allowed an insight into PUR behaviour upon ageing at both the molecular and visual (micro) levels. For each class (i–v), PURs showing condition grades ranging from fair to unacceptable have been included[63]. Consequently, different stages of PUR ageing have been assessed, making possible to correlate each condition to specific PUR changes in the IR spectrum and PUR surface (by micro observation). Each condition was at least characterised based on two historical objects (or independent areas from one single object), and six micro samples (three per each object/area).

To carry out this task, model samples[64] for (i–iv) have been produced (serving as unaged samples) and compared to the respective case studies[65]. The production of the models has followed typical formulations of ether- and ester-based PUR slabstock foams, ether-based PUR moulded foams (cold process) and ester-based TPU films (see Appendices I and IV). For (ii) and (iii), additional references of naturally aged foams were included to fulfil missing data (lack of objects representing specific condition grades).

As systematic differences have been identified between the historical objects (according to condition grades) and the unaged models, a visual and molecular deterioration course was potentially revealed, making possible to suggest a visual and IR ageing pathway for each PUR (i–iv). To verify the reproducibility of the detected differences, each model was submitted to both artificial (light, λ>300nm) and natural (outdoor) ageing conditions. Regarding the environmental exposure conditions

[63] As mentioned before, this thesis follows the condition scale proposed by the European Popart Project: good, fair, poor and unacceptable (Lavédrine *et al*., 2012a: 297).
[64] See Appendices I and IV for more details.
[65] This approach was only performed for PUR foams and coatings as only two of the selected case studies showed TPU fibres.

of the selected objects to date, the presence of oxygen, fluctuating moisture and temperature (≈10–30°C) should be considered for all selected case studies (and respective PURs). Light, on the other hand, althought expected to be one of the main deterioration agents (especially for ether-based PURs), in some cases, it has been filtered by more or less dense physical barriers[66]. Thus, for some of the selected historical PURs, light could have been filtered (in different extents) or even absent. Still, with the attempt to (i) design an experimental representing the general ageing tendency of the case studies, (ii) to "accelerate" PUR degradation (in the unaged references), and (iii) to avoid ageing conditions distant from representative environments (such as high T, which could induce thermal degradation reactions), light was present in both ageing experiments. The outdoor ageing has been selected due to the possibility of studying the influence of natural and fluctuating conditions (especially, fluctuating RH) on PUR ageing.

For the natural ageing, the references were submitted to an outdoor environment (3–4 four hours of direct sun light, 60–100% RH and c. 5–20°C)[67] until yellowing and structural weakness (high susceptibility to handle, in the case of foams) were observed, which was clearly achieved after five months of exposure.

For the artificial ageing, samples were submitted to UV-Vis radiation using a light ageing chamber equipped with a cut off filter below 300 nm (simulating indoor exposure, λ>300 nm, c. 25°C) during seven days. After seven days of exposure (total amount of irradiance: 483 MJ/m^2), yellowing and structural weakness were clearly shown. Although it would be beneficial to establish a correlation factor between the total amount of irradiance of the artificial exposure and real time exposure, Feller stated that 'this will depend more on the materials involved, as well as temperature and humidity, rather than intensity of irradiance alone' (Feller, 1994: 97). As PUR is highly prone to deterioration, non-linear rates of degradation are expected. For that reason, a plausible value for this correlation was not possible to establish.

The assessment of the ageing experiments was carried out using IR μ-spectroscopy and optical microscopy (OM) after one and a half, three and five months for the outdoor ageing; and after two, five and seven days for the artificial ageing. Three spectra were recorded from three independent micro samples collected at the surface of each sample.

The following sections discuss the results of each PUR type and form. Firstly, an insight into the characterisation of the models is given, following to the in-depth analysis of the case studies. Correlations between PUR condition and both infrared and visual pathways of PUR are proposed, and finally, aged references are compared to the case studies. Hydrogen-bonding interactions (H-bonds)

[66] For example, in foam cushioning objects where PUR foams are used underneath fabric textiles or opaque plastic covers, or even covered by thick paint layers.

[67] For more details, see Appendix I.

are studied in detail by following the carbonyl function absorptions in the infrared and visual changes at the micro level.

3.3. Ether-based PUR foams

3.3.1 Ether-based PUR slabstock foams

3.3.1.1 Model sample of ether-based PUR slabstock foam

A visual insight for the unaged model is shown in Fig. 3.1. Its good condition is evident by the bright whitish colour as well as by the presence of defectless cell struts (Fig. 3.1a,b). The open-cell bun can be described as colourless/white, bright, and with regular outline shapes and smooth texture (with no irregularities or imperfections).

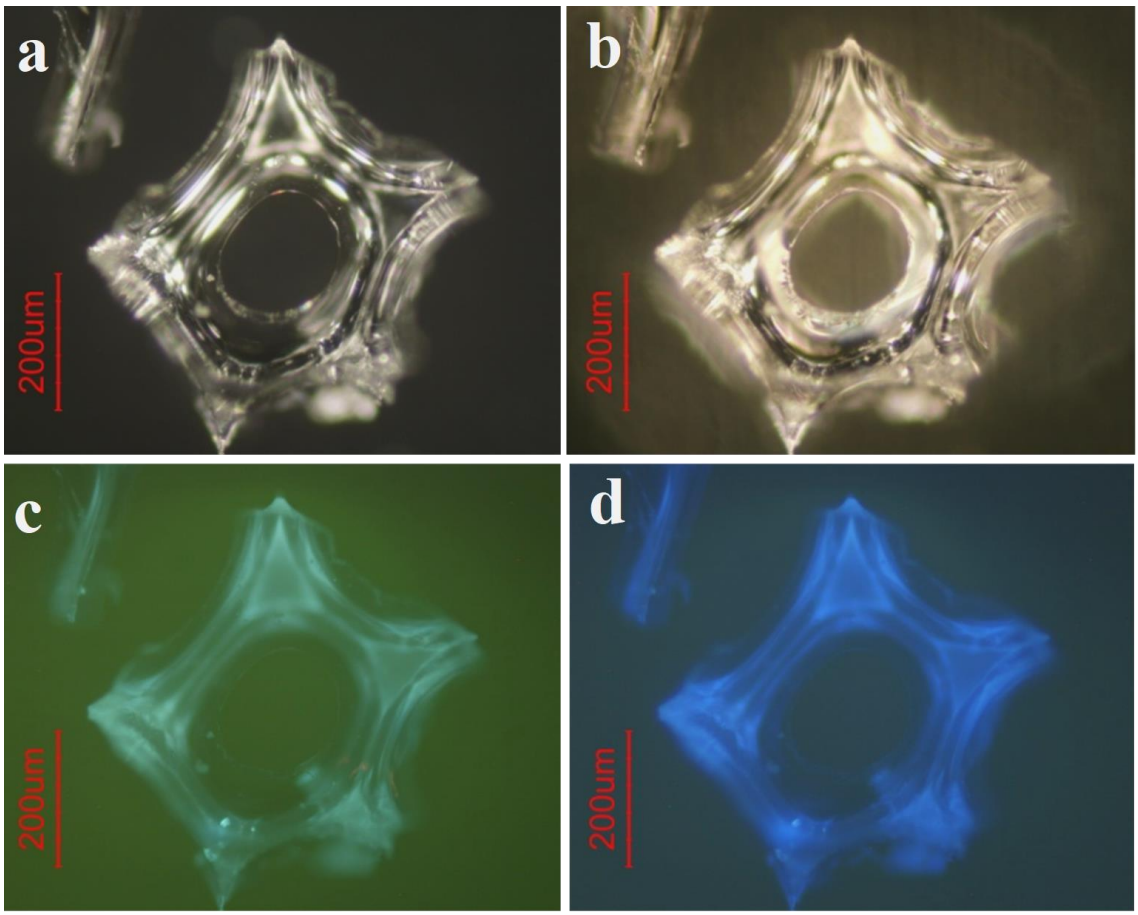


Figure 3.1 Microscopy images of the model PUR slabstock foam cell bun under reflected cross-polarised light (a), darkfield (b), blue-violet light (c) and ultraviolet light (d).

In addition, this foam shows a weak fluorescence under longer (blue-violet light) and shorter (ultraviolet light) wavelengths (Fig. 3.1c,d). This fluorescence could be attributed to the presence of aromatic structures and amide groups in PUR foam molecular network (see Chapter 1, section 1.1.2). According to Rost, aromatic rings and amides are known to be responsible for the green (flavins bonded to proteins under blue light) and blue (protein compounds under ultraviolet light) fluorescence of animal and plant tissues (Rost, 1995). In common with PURs, flavins and proteins are also rich in aromatic structures and amide groups, which could justify the same fluorescence behaviour. From previous studies concerning the fluorescence of aged polymers, the presence of aromatic fluorophores was also mentioned to cause the fluorescence emission of polymers (Comelli *et al*., 2014; Nevin *et al*., 2014). The weak fluorescence intensity observed in the unaged reference could be justified by the redox state of these compounds. According to Aubin's study about the autofluorescence of cells, the fluorescence intensity of these compounds depends on the redox state of the cell (Aubin, 1979 as cited in Rost, 1995: 3). For example, only the oxidized forms of flavoproteins are fluorescent and these compounds are very sensitive to light (Aubin, 1979 as cited in Rost, 1995: 3, 4). Since the PUR reference shows a good condition, the weak fluorescence intensity may be associated to the predominance of non-oxidized forms.

From infrared spectroscopy and according to the literature, the slabstock reference spectrum[68] shows the characteristic bands of water-blown polyether-based polyurethane foams (Fig. 3.2) (Priester *et al*., 1990; Elwell *et al*., 1996; Wilhelm & Gardette, 1998; Wilhelm *et al*., 1998). The absorption band at 1107 cm^{-1} corresponds to the stretching vibration of C–O–C groups from the ether-based soft-segment (SS). The presence of aromatic diisocyanate structures is confirmed by the absorption bands at 1600 cm^{-1} (C–C quadrant stretching of aromatic ring), 1537 cm^{-1} (C–N stretching and N–H bending of amide II) and between 870–700 cm^{-1} (C–H wag and C–H bending of benzene ring). The region between 3500–3200 cm^{-1} is ascribed to the N–H stretching region from the hard-segment and between 2971–2867 cm^{-1} to the C–H stretching region of both hard- and soft-segments (HS and SS). The carbonyl group (amide I) shows infrared absorptions between 1800–1600 cm^{-1} and provides information regarding hydrogen-bonding interactions (Fig. 3.2, inset). The band at 1727 cm^{-1} is assigned to the C=O stretching absorption from urethane linkages (free of hydrogen-bonding) and the absorption at 1643 cm^{-1}, to the C=O stretching from urea linkages (strongly H-bonded, bidentate urea) (Priester *et al*., 1990; Elwell *et al*., 1996). The shoulder at 1712 cm^{-1} confirms the presence of some loosely associated urethane and/or non-associated urea (Priester *et al*., 1990; Elwell *et al*., 1996). In relation to the N–H stretching region, the absorption at c. 3500 cm^{-1} corresponds to the N–H free of hydrogen-

[68] See Appendix IV for a complete assignment of IR bands.

bonding and at c. 3330 cm^{-1} to the H-bonded N–H stretching. The presence of the band at 1643 cm^{-1} confirms the ordered structure of the HS as commonly found in typical PUR slabstock foams

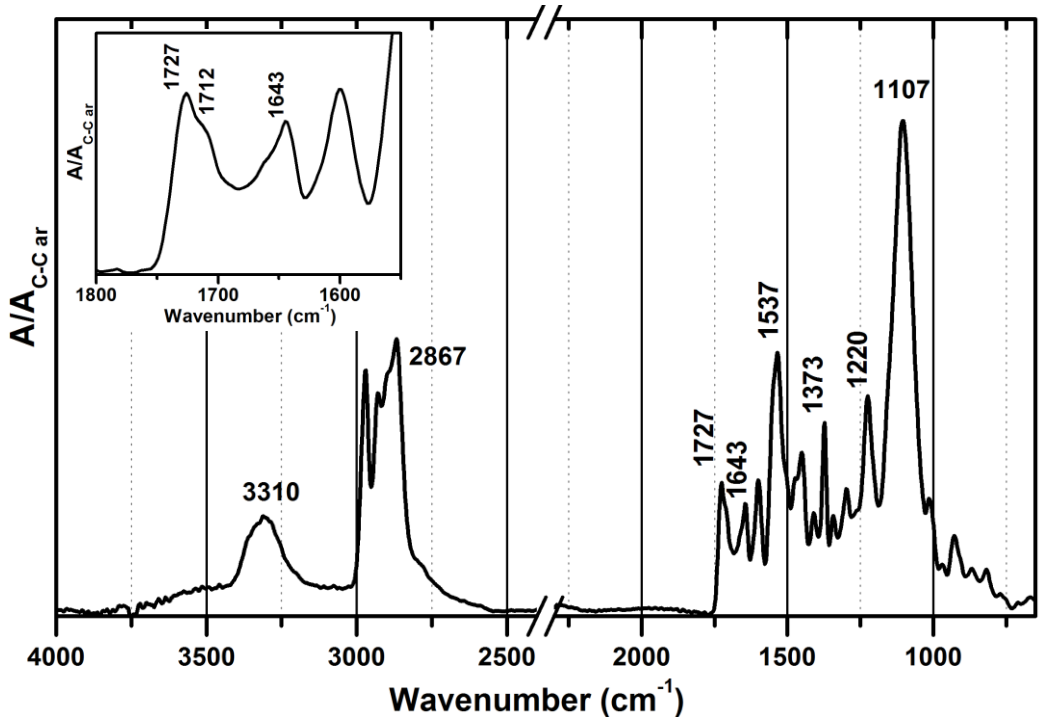


Figure 3.2 Infrared spectrum of the model PUR slabstock foam. Inset: Detail of the carbonyl region from 1800 to 1550 cm^{-1}.

3.3.1.2 Historical ether-based PUR slabstock foams

From the study of ten historical objects from the MUDE collection based on TDI and polyether-based polyols, five representative case studies dated between the 1960s and 1970s are discussed (Fig. 3.3 and Fig. 3, page 4)[69]. The selected set is composed of PUR foams showing conditions from fair to unacceptable: *Superonda* and *Bocca* foams are examples of fair condition (slight yellow colour and physical stability when handled); *Djinn* and *Amphys* of poor condition (yellow colour and susceptibility to rupture when handled); and *Safari* of an unacceptable condition (yellow and brown colours and high level of crumbling) (Fig. 3.4). Apart from the PUR foam from *Safari*, each case study showed homogeneous macroscopic properties at the foam surface[70]. The PUR foam from *Safari* showed a high level of crumbling and three different colours (one yellow and two browns, as shown in Fig. 3.4).

[69] Enlarged images of the objects are shown in Appendix III.

[70] Regarding this aspect, it is important to emphasise that the deterioration of ether-based PUR flexible foam is not completely homogeneous throughout the entire depth of the foam, i.e., the deterioration at the surface does not show the same grade as the interior layers. In general, the most interior layers of the foam are more stable than the outer layers due to the limited interaction of oxygen and light (main deterioration agents for this type of PUR) with the polymer. This fact has been already discussed by authors such as Thea van Oosten and Dan Rosu *et al.* (van Oosten, 2011; Rosu *et al.*, 2009).

Since the case studies were probably produced in closer periods of time and their incorporation into the museum's collection happened at the same time (2002), three hypotheses were considered to justify their different condition: (i) different foam formulations (ii) different object biographies before their incorporation into the museum's collection and (iii) different covering materials. In relation to the first hypothesis, although their infrared spectra indicated similar PUR formulations, the presence of additives was not possible to identify, probably due to their low concentration (under 3%) (Lavédrine *et al*., 2012b: 105). Regarding the object´s biographies until 2002, it is likely that some of these items had served their daily function in the past. However, it was not possible to have access to that information and to establish a correlation with their condition. On the other hand, in relation to the different covering materials, a good relationship was established. The PUR foams from *Superonda* and *Bocca* sofas (Figs. 3.3 and 3.5a,b) were selected as case studies presenting a fair condition. In the former, the PUR foam is covered by a thick black vinyl fabric (PVC) and in the second, by a dense weave elastic fabric (Fig. 3.3). These two covers could have acted as preventive barriers for PUR foam deterioration. As case studies indicative of poor condition grades, *Djinn* and *Amphys* sofas were chosen (Figs. 3.3 and 3.5c,d). In these cases, less weaved fabrics were used and as a result, the deterioration rate has been higher. The last selected case study, an example of an unacceptable condition grade, was the *Safari* sofa (Figs. 3.3 and 3.5e,f). For this object and according to the testimony of Roberta Meloni from the Centro Studi Poltronova (*Safari*'s production company), a Pirelli's foam was used, along with an adhesive to adhere the foam to the animal print textile (R. Meloni, written interview, March 23, 2014). This foam, due to its highly-perforated plates (described as 'Swiss cheese') made it possible to use PUR foams in curved shapes. Thus, the presence of a highly-perforated foam plate (less dense and thick) may have accelerated the deterioration rate of this object. From this perspective, the objects conditions (ranging

Figure 3.3 Polyether-based PUR slabstock foam case studies from the MUDE collection. From top to bottom: *Superonda* (1966), *Bocca* (1971), *Djinn* (1965) and *Amphys* (1968). Photos: ©MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

from fair to unacceptable) are justified based on the exposure degree of the PUR foams to deterioration agents for the last circa fifty years.

Figure 3.4 Loss of elasticity, fragile network and different yellowing grades found on the PUR foam from the *Safari* upholstery. From left to right: yellow, brown and dark brown.

The different conditions showed by the selected objects are clearly visible based on optical microscopy (Fig. 3.5). In contrast with the unaged reference (Fig. 3.1), it is possible to conclude that upon ageing, the cell bun becomes yellow and brown, looses transparency and shine and gains irregularities in its texture (Fig. 3.5). From darkfield microscopy, topography and brightness are highlighted due to the oblique rays illuminating the specimen and light effects such as diffraction, reflection and refraction (Davidson & Abramowitz, 2002). This illumination mode is especially used 'for revealing outlines, edges, and boundaries' (Davidson & Abramowitz, 2002: 26), and in this case, for revealing superficial damages on the polymer cell buns. As examples of physical deterioration aspects on PUR foams upon ageing, micro holes (Fig. 3.5a,b), disruptions on the cellular shape outline (Fig. 3.5c), cracks crossing the cell struts (Fig. 3.5d–f) and pitting (Fig. 3.5e–g) are observed. The last two (cracks and pitting) are mostly found on poor and unacceptable conditions (Fig. 3.5d–g), while holes and minor cracks appeared in less deteriorated grades. Figure 3.6 shows details of the damages, as found on the case studies.

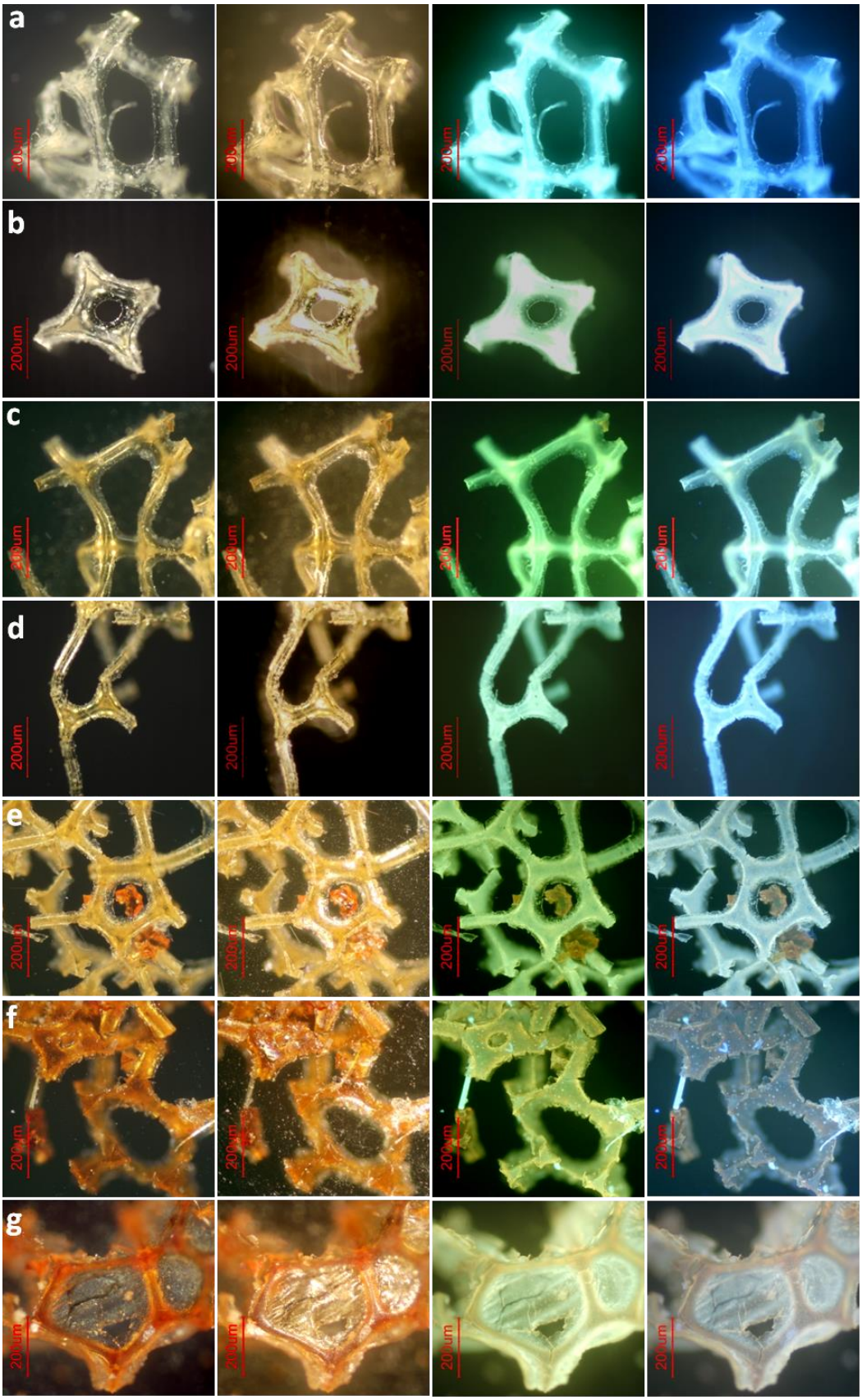


Figure 3.5 Microscopy images of PUR slabstock foam cell buns collected from the historical objects showing different condition grades. From left to right: under reflected cross-polarised light, darkfield, blue-violet light and ultraviolet light. Fair condition grade: *Superonda* (a) and *Bocca* (b). Poor condition grade: *Djinn* (c) and *Amphys* (d). Unacceptable condition grade: *Safari*, yellow foam (e) and brown foams (f, g). The cell buns from (g) were

collected from the foam surface of *Safari* and show the deposition of the adhesive (film) inside the cell struts. Although these cell buns show visual similarities with PUR closed cell buns or PUR skins, the infrared spectrum did not show any absorption band between 1500–1530 cm^{-1} (amide II), characteristic of PURs.

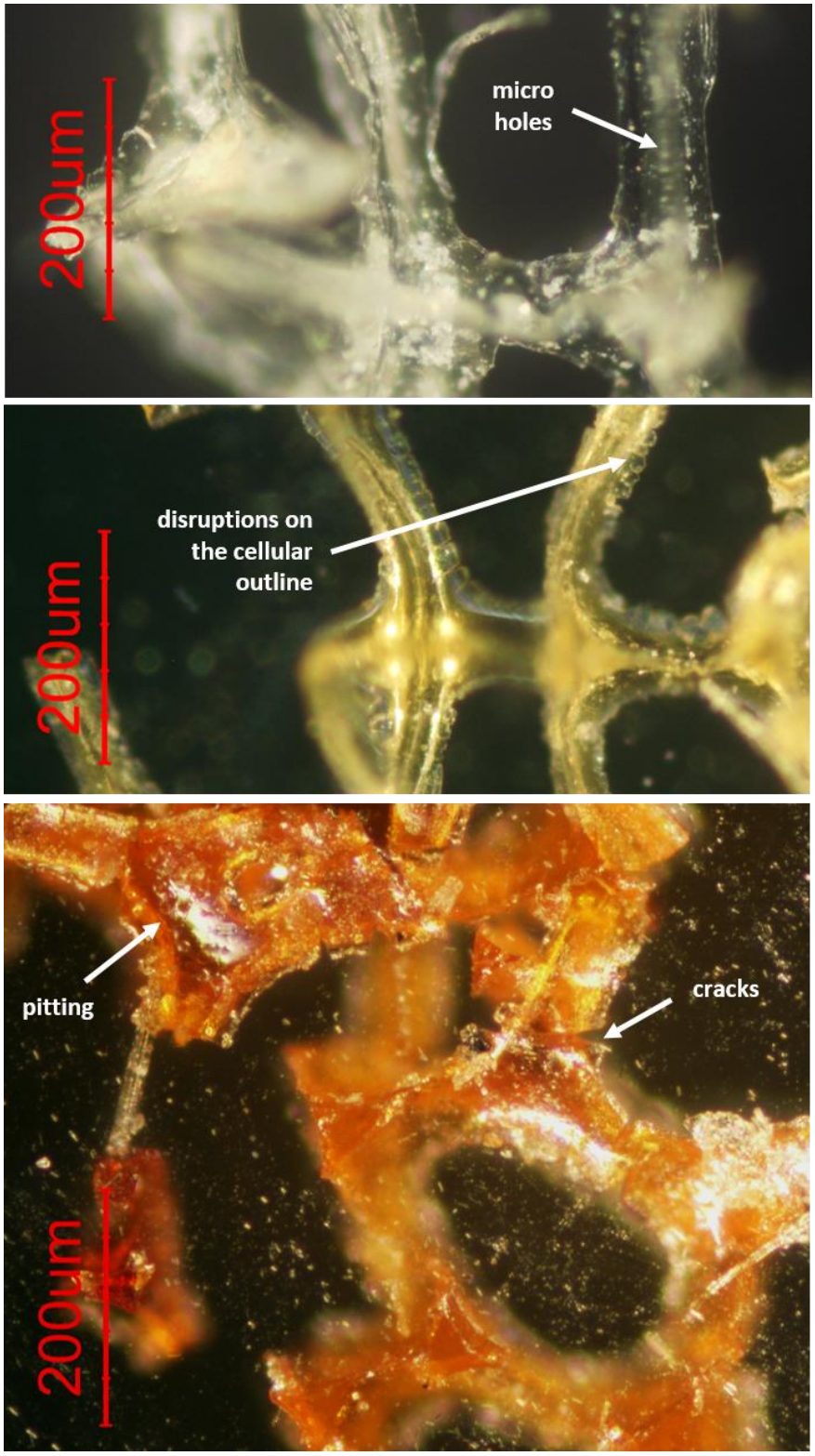


Figure 3.6 Selected details of the damages found on the case studies foams under reflected cross-polarised (top and middle) and darkfield (bottom) light.

Regarding the microscopy images under blue-violet and ultraviolet light (Fig. 3.5, on the right), finer resolution was obtained and the physical aspects become clearly visible. This fact is explained by the use of shorter wavelengths than visible light (Rost, 1992). The fluorescence behaviour of the PUR historical objects also changed in relation to condition grades. While the unaged reference showed a weak fluorescence, the aged objects are highly fluorescent when irradiated with both blue-violet and ultraviolet light, especially, when the yellowing degree increased. According to previous studies concerning the use of fluorescence spectroscopy for the characterisation of aged polymers, the formation of conjugated double bonds (causing yellowing), deterioration products from protein compounds and modifications on the microenvironment surrounding fluorescent species (such as aromatic rings) gave rise to fluorescence bands that were not present on the unaged references (Nevin *et al*., 2014; Toja *et al*., 2013; Comelli *et al*., 2014). Consequently, the increased fluorescence intensity observed on the PUR historical objects could be associated to the formation of these species, and to the redox state of the polymer (as previously mentioned). The fluorescence under blue-violet light may have revealed the presence of different chromophores in samples which showed identical yellow colour shades as different colours are emitted (Fig. 3.5c,d under cross-polarised light). This may give emphasis to the higher sensitivity of the blue-violet wavelength to the formation of conjugated double bond systems than ultraviolet light.

From IR spectroscopy, it was possible to identify spectral changes correlated with the deterioration of PUR structure. According to Fig. 3.7, from the unaged reference (black) to the highly-deteriorated foams (grey spectra, Fig. 3.7e–g), several spectral changes are detected in the N–H, C–H and C=O stretching regions. The first clear spectral change is the relative intensity decrease of the C–H stretching absorptions between 2971–2867 cm^{-1} (Fig. 3.6a–g). Along with this change, the decrease of the ether C–O–C stretching absorption at 1107 cm^{-1} is also observed. This finding, pointing out the scission of SS chains and consequent formation of oligomers is in accordance with the literature (Wilhelm & Gardette, 1998; Wilhelm *et al*., 1998), and could be related to the amorphous structure of the polyol in the polymer network (easier interaction of oxygen and moisture). Polyether polyols used in flexible foams have functionalities in the range of 2.5–3.1 (Oertel, 1985; Saunders & Frisch, 1962) and a star shape molecular chain structure (Ionescu & Petrovic, 2010). As a result, the instability of ether bonds is high and their own presence in the PUR network induces the production of radicals. Concerning the N–H stretching bands, both fair and poor condition grades spectra do not show significant changes in this region (3500–3200 cm^{-1}) (Fig. 3.7a–d).

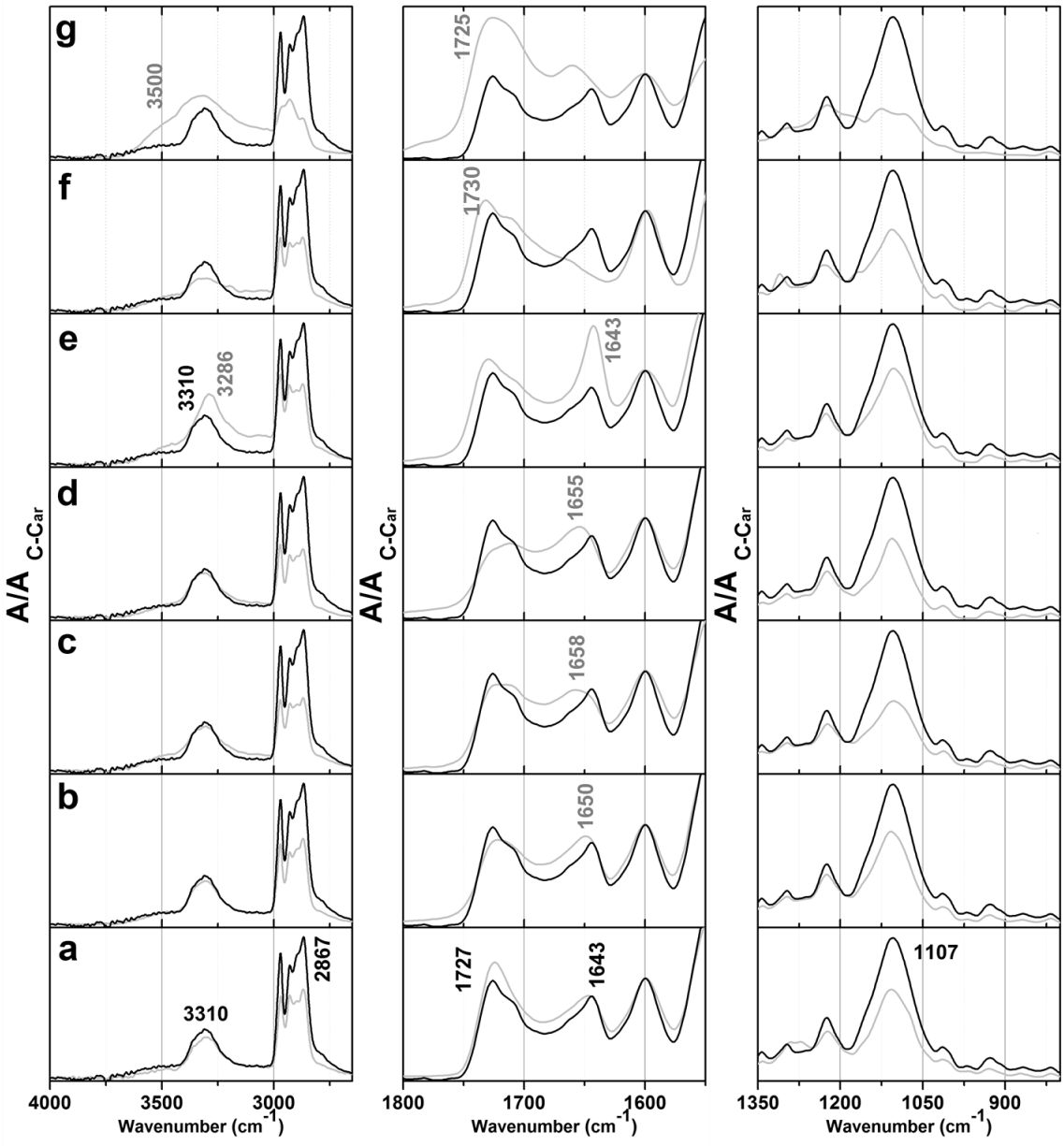


Figure 3.7 Infrared spectra of the unaged model PUR slabstock foam (black) and the PUR foams from the case studies from the MUDE collection (grey) showing different condition grades: N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). Fair condition grade: *Superonda* (a) and *Bocca* (b). Poor condition grade: *Djinn* (c) and *Amphys* (d). Unacceptable condition grade: *Safari*, yellow foam (e) and brown foams (f, g).

On the other hand, the carbonyl region (1800–1600 cm^{-1}) shows several spectral changes right at fair conditions. The C=O absorption band at c. 1640 cm^{-1} (bidentate urea) loses intensity and shifts to higher frequencies (monodentate urea) (Fig. 3.7a–d, centre) (Priester *et al*., 1990). This shift could be attributed to the weakening of the hydrogen-bonding interactions between HS chains and to the consequent disarrangement of this domain. The PUR foams presenting unacceptable conditions show major spectral changes in both regions (N–H and C=O stretching absorptions). In the severely yellowed

and deteriorated foam from *Safari* (Fig. 3.7e), the relative intensity of the N–H band (previously centred at c. 3310 cm^{-1}) increases and shifts to lower frequencies (to c. 3285 cm^{-1}, possibly caused by the formation of new hydrogen-bonding interactions in the HS) and the band between 3500–3400 cm^{-1} shows a slight increase (attributed to the formation of oxidation products such as hydroperoxides, alcohols and carboxylic acids) (Dannoux *et al*., 2005; Wilhelm *et al*., 1998). In the respective carbonyl region (Fig. 3.7e, on the centre), a strong increase of the relative intensity at c. 1640 cm^{-1} (bidentate urea) is observed, which corroborates the previous hypothesis. It is also possible to observe that the C=O band at c. 1725 cm^{-1} shows a slight shift (to higher frequencies, 1730 cm^{-1}) and broadening. This could corroborate the formation of carboxylic acidic species and formats due to the scission of SS chains (Dannoux *et al*., 2005; Wilhelm *et al*., 1998). From the infrared spectra of the most degraded PUR object (Fig. 3.7f,g) it is further suggested that higher deterioration levels are reflected by: the elimination of the urea band at c. 1640 cm^{-1} and decrease of the relative intensity of the 3400–3200 cm^{-1} region (Fig. 3.7f); or, to the higher increase of the C=O relative intensity at c. 1725 cm^{-1} and of both O–H and N-H groups between 3630–3100 cm^{-1} (Fig. 3.7g). In the first case, these changes are attributed to the loss of associated C=O and N–H (from urea linkages) and in the second case, to the formation of oxidation products such as hydroperoxides, alcohols and carboxylic acids. In both cases, the total collapse of the PUR foam was observed.

From this approach, a new insight into PUR foam deterioration is suggested based on prospective relationships between visual aspects and molecular fingerprints of the PUR historical objects. The first visual signs of PUR foam physical deterioration (slight yellowing, loss of transparency and formation of micro holes), may be related to the chain scission of the ether-based SS and to the formation of additional chromophores. The development of micro cracks and ruptures on the cell bun may be a consequence of the elimination of some hydrogen-bonding interactions between HS chains, in addition to the previous mentioned molecular changes. Finally, the cell bun embrittlement and the formation of cracks, which completely cross the cell strut, and the presence of pitting may be the result of drastic modifications on the secondary bonds. These physical changes could also reflect the complete disintegration of the foam structure.

As these samples come from different objects with possible different formulations and biographies, the following section validates the obtained results with ageing experiments carried out on reference samples.

3.3.1.3 Ageing experiments for the model sample

The unaged model was submitted to natural (outdoor) and artificial (UV-Vis radiation, λ > 300nm) ageing experiments. Based on optical microscopy (OM), a visual decay similar to that of the PUR historical objects was observed (Figs. 3.8 and 3.9).

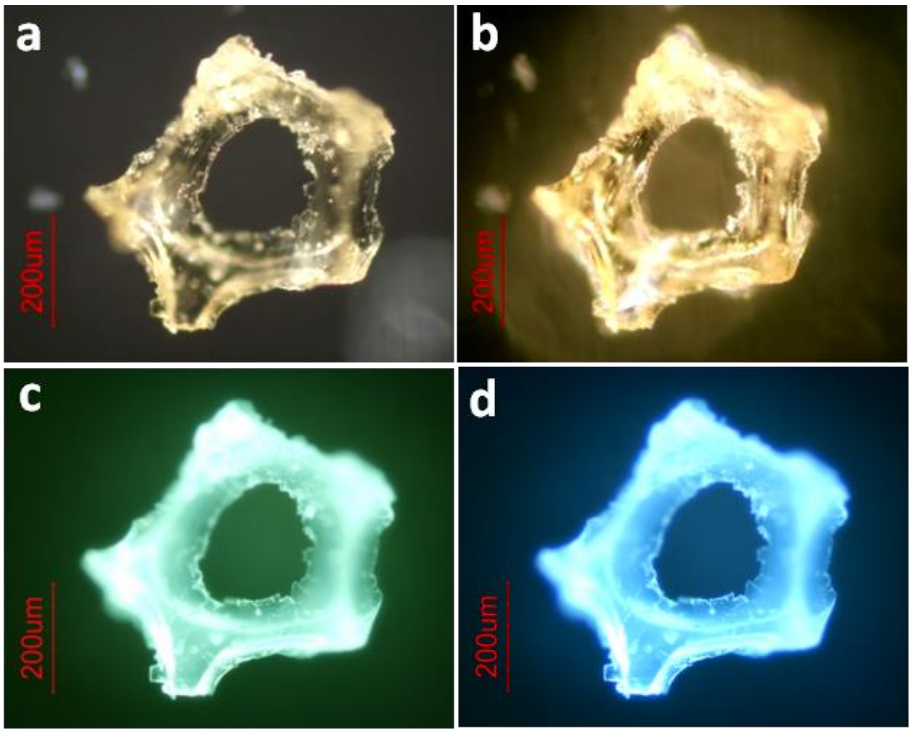


Figure 3.8 Microscopy images of the model PUR slabstock foam cell bun after three months of natural (outdoor) ageing under reflected cross-polarised light (a), darkfield (b), blue-violet light (c) and ultraviolet light (d).

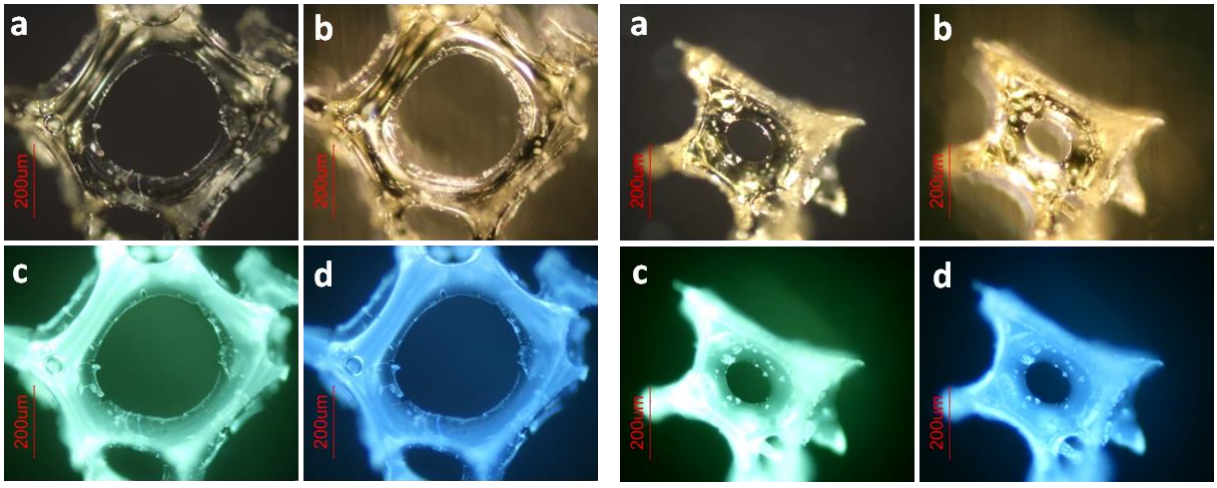


Figure 3.9 Microscopy images of the model PUR slabstock foam cell bun after two (left) and five (right) days of artificial ageing (UV-Vis radiation, λ>300nm) under reflected cross-polarised light (a), darkfield (b), blue-violet light (c) and ultraviolet light (d).

For the model sample exposed to outdoor conditions, yellowing and loss of transparency were already observed after one and a half months of ageing, and the formation of micro holes, pitting and cracks, were clearly visible shortly after three months (Fig. 3.8). Nevertheless, cracks crossing the cell struts have not been found in the naturally (outdoor) aged model as in the PUR foams from the historical case studies. Regarding the artificially aged samples, although yellowing and loss of transparency were detected shortly after 2 days of exposure, the continuity of the experiment led to the development of physical damages more distant from the historical objects (Fig. 3.9). For example, although some disruptions and minor cracks were observed, deep pitting was the most common deterioration aspect (Fig. 3.9a–d, on the right). For this reason, it is believed that minor cracks and fractures crossing the entire cell strut may be a consequence of longer exposures and possible handling, which did not happen to the model during the ageing experiments.

Regarding the fluorescence microscopy images, a gain in intensity was observed (Figs. 3.9c,d compared to 3.2c,d), and these samples emitted identical colours as the PUR foam from the *Amphys* sofa (Fig. 3.5d, on the right). This may enable to establish some correlation between the results from the characterisation of the PUR objects and the ageing experiments.

In general, we may conclude that the model exposed to outdoor conditions showed more comparable visual aspects with the ones found in the historical case studies.

From the infrared results, it was also possible to identify comparable ageing pathways between the ageing experiments (Figs. 3.10 and 3.11) and the historical objects (Fig. 3.7). In all cases there was a decrease of both C–H stretching bands between 2971–2867 cm^{-1} and C–O–C stretching band at 1107 cm^{-1}, an increase and shift to lower frequencies of the N–H band (centred at 3286 cm^{-1}) and an increase of the band between 3500–3400 cm^{-1} (Fig. 3.7a–f compared to Figs. 3.10 and 3.11, on the left). In relation to the carbonyl region (Fig. 3.7a–f compared to Figs. 3.10 and 3.11, on the centre), it is also possible to suggest that the infrared ageing course of the C=O stretching band from urea linkages (at c. 1640 cm^{-1}) is comparable in all cases (historical objects and aged models), but the C=O stretching band from urethane (at c. 1727 cm^{-1}) shows a higher intensity increase, especially in the artificial light ageing. This difference might result from the presence of Vis and UV radiation upon the two ageing experiments, which as previously explained, could have been filtered during the objects' foams ageing. As mentioned in the literature, the photodegradation of the ether-based SS leads to the formation of hydroperoxides, formats and carboxylic acids. Therefore, the higher intensities of the C=O infrared fingerprint between 1780–1725 cm^{-1} (i.e. increase of a band at c. 1730 cm^{-1} and appearance of a band at c. 1780 cm^{-1}) may result from this variance.

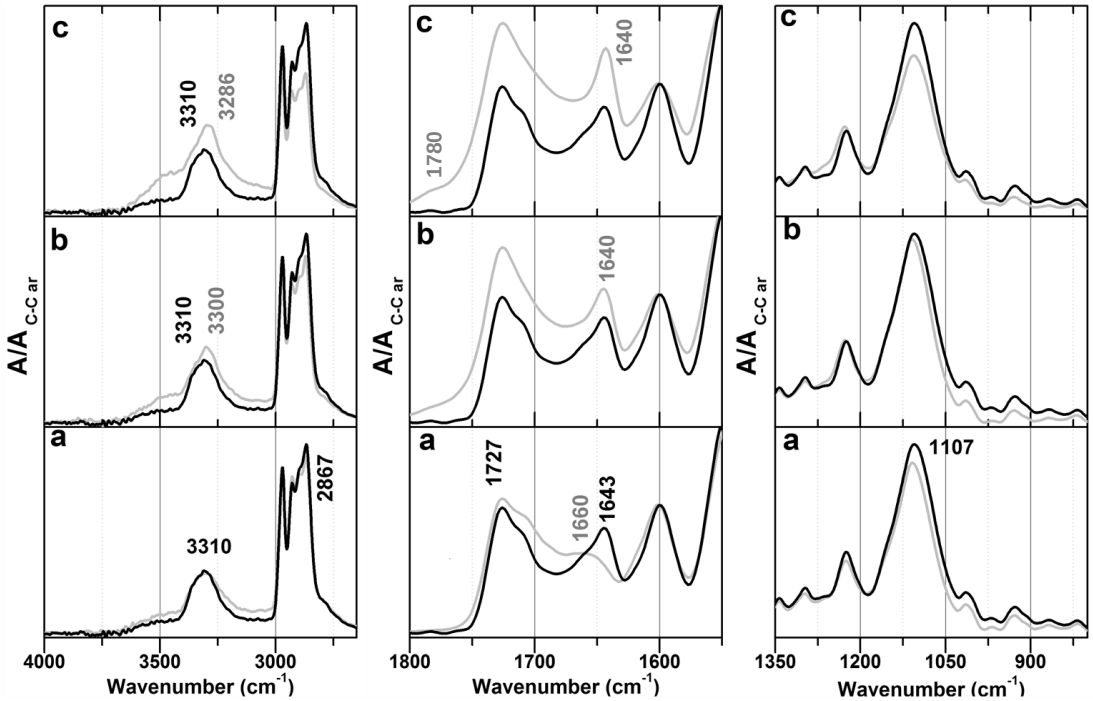


Figure 3.10 Infrared spectra of the model PUR slabstock foam before (black) and after (grey) natural ageing (outdoor): N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). After one and a half months (a), after three months (b) and after five months (c).

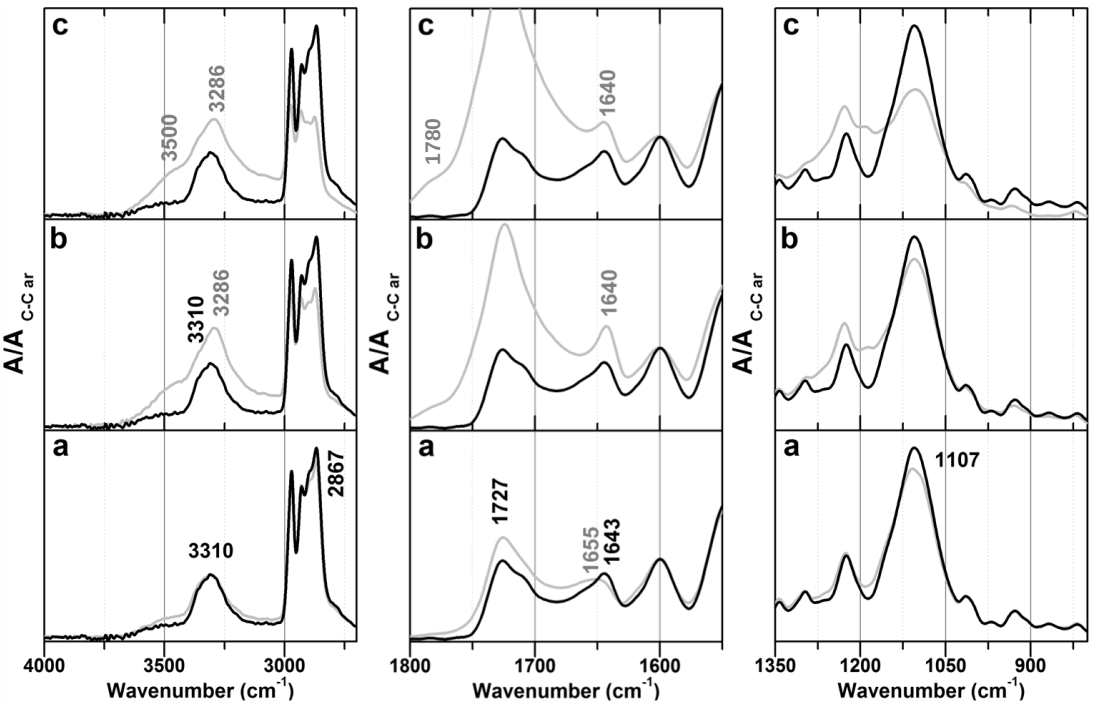


Figure 3.11 Infrared spectra of the model PUR slabstock foam before (black) and after (grey) artificial ageing (UV-Vis radiation, λ > 300 nm): N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). After one and a half months (a), after three months (b) and after five months (c).

Regarding the urea C=O stretching band (and as in the case studies), at first there is a decrease of its relative intensity and shift to higher frequencies (≈1660 cm^{-1}), followed by a return to its first frequency at c. 1640 cm^{-1} and finally, a large increase in relative intensity (from 0.75 to 1.27, i.e. almost doubles its absorbance). The band at c. 1640 cm^{-1} from the *Safari* foam (Fig. 3.7e, on the centre) shows a closer relative intensity.

These values along with the previously mentioned spectral changes might validate the hypothesis of the deterioration of PUR hard domain ordered structure during ageing, by the modification of the hydrogen-bonding interactions between HS chains. The hard domains on PUR segregated structure are rich in polyurea segments. Although these segments represent the rigid phase of the polymer network morphology, they have branched structures and therefore, are susceptible to deterioration. As previously mentioned, H-bonds between urea linkages are labile at high temperatures and high relative humidity. For that reason, in this paper it is suggested that the deterioration path of PUR foam (polyether based) upon ageing could be (i) the elimination of some hydrogen-bonding interactions (reflected in the IR spectra by the shift of bidentate urea to monodentate urea) and the formation of a disordered HS domain which enables (ii) the penetration of water molecules by osmosis as well as the interaction of oxidation products into the free space between the HS chains and (iii) the formation of new hydrogen-bonding interactions between these compounds and the urea groups (reflected in the IR by the large increase of bidentate urea relative intensity). A schematic representation of these steps was designed and shown in Fig. 3.12. Since high relative humidity and temperature have been mentioned as a possible cause for the modification of H-bonds between HS chains, the high RH values (RH>60%) during the outdoor ageing, and the higher T (c. 25°C) and intense UV-Vis radiation of the artificial ageing may have acted as deterioration agents for this foam. Regarding the outdoor ageing, a cylinder of hydration could be formed around the HS chains with new hydrogen-bonding interactions being formed between urea and water molecules. As the objects have been kept in the dark since 2002 (in museum storage), their foams are underneath textile fabrics or opaque plastics (not directly exposed to light), and the PUR H-bonds in both case studies and aged references suffered the same degradation pattern, this study alerts for the importance of controlling RH in the preservation of ether-based PUR foams, or, to the fact that the exclusive presence of oxygen can be sufficient to disrupt these secondary bonds. Furthermore, due to the spectral evolution of the urea stretching vibration at c. 1640 cm^{-1} (described above), this band can be used as an IR marker of PUR flexible foams condition, when analysed in relation to the stable aromatic band at c. 1600 cm^{-1}: PURs in good condition show a band at c. 1640 cm^{-1} with lower intensity than the band at c. 1600 cm^{-1}; PURs in fair condition show a band between 1645–1640 cm^{-1} with lower intensity than the band at c. 1600 cm^{-1}; PURs in poor conditions show a band between 1660–1650 cm^{-1} with lower intensity than the band at c. 1600 cm^{-1};

and PURs in unacceptable condition show a band at c. 1640 cm^{-1} with higher intensity than the band at c. 1600 cm^{-1}, or, no band between 1675–1630 cm^{-1}.

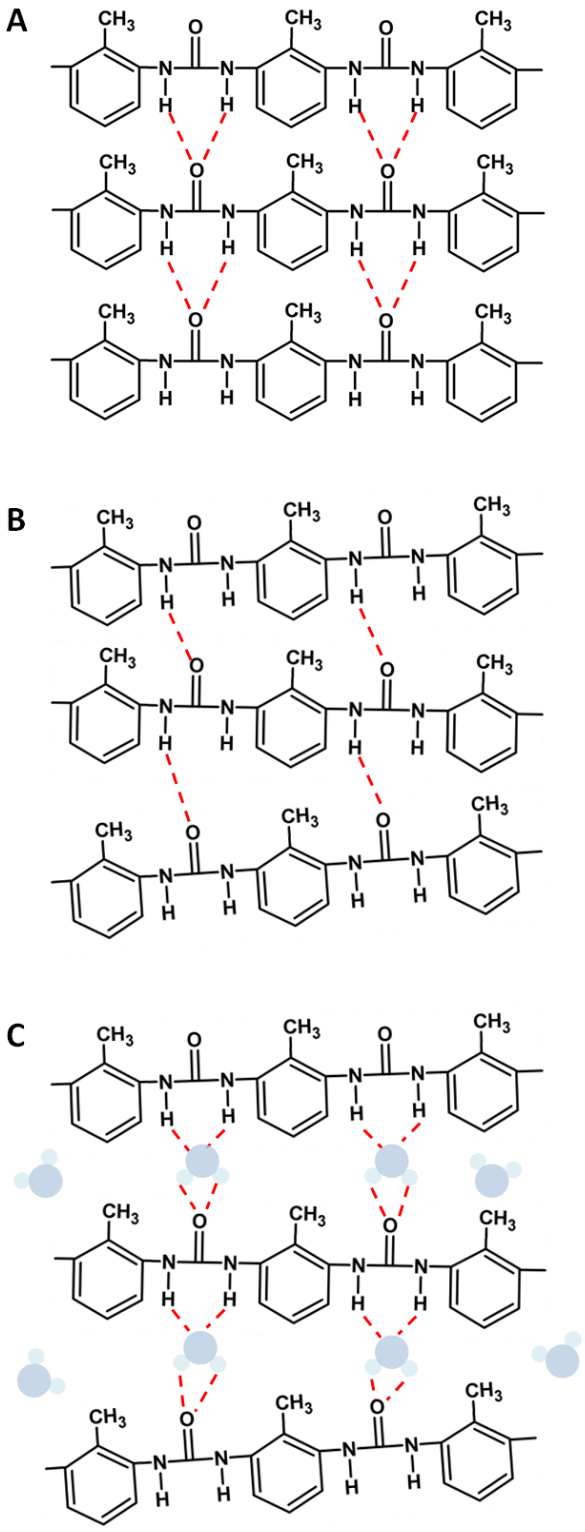


Figure 3.12 Deterioration course of hydrogen-bonding interactions in PUR slabstock foams HS domain. Schematic representation of hydrogen-bonding interactions (red dash line) deterioration in PUR HS domains (not shown to scale). HS domain in PUR foams in unaged/good condition (A), in aged/poor condition (B) and in aged/unacceptable condition (C).

As PUR moulded foams have been described as having a different micro morphology at t=0 (shorter and less ordered HS domains), the following section intends to understand if this difference results in different PUR deterioration courses that, in turn, could influence the selection of preventive measures for PUR moulded foams in museum collections.

3.3.2 Ether-based PUR cold-moulded foams

3.3.2.1 Model sample of ether-based PUR cold-moulded foam

Since similarities were found between moulded and slabstock ether-based PUR foams, only main differences are highlighted in this section.

A visual insight for the unaged model of cold-moulded PUR foam is shown in Fig. 3.13. Similarly to the previous case, the good condition of the model is reflected by bright and defect less cell struts (Fig. 3.13a,b). Still, some differences could be noticed in relation to the slabstock model.

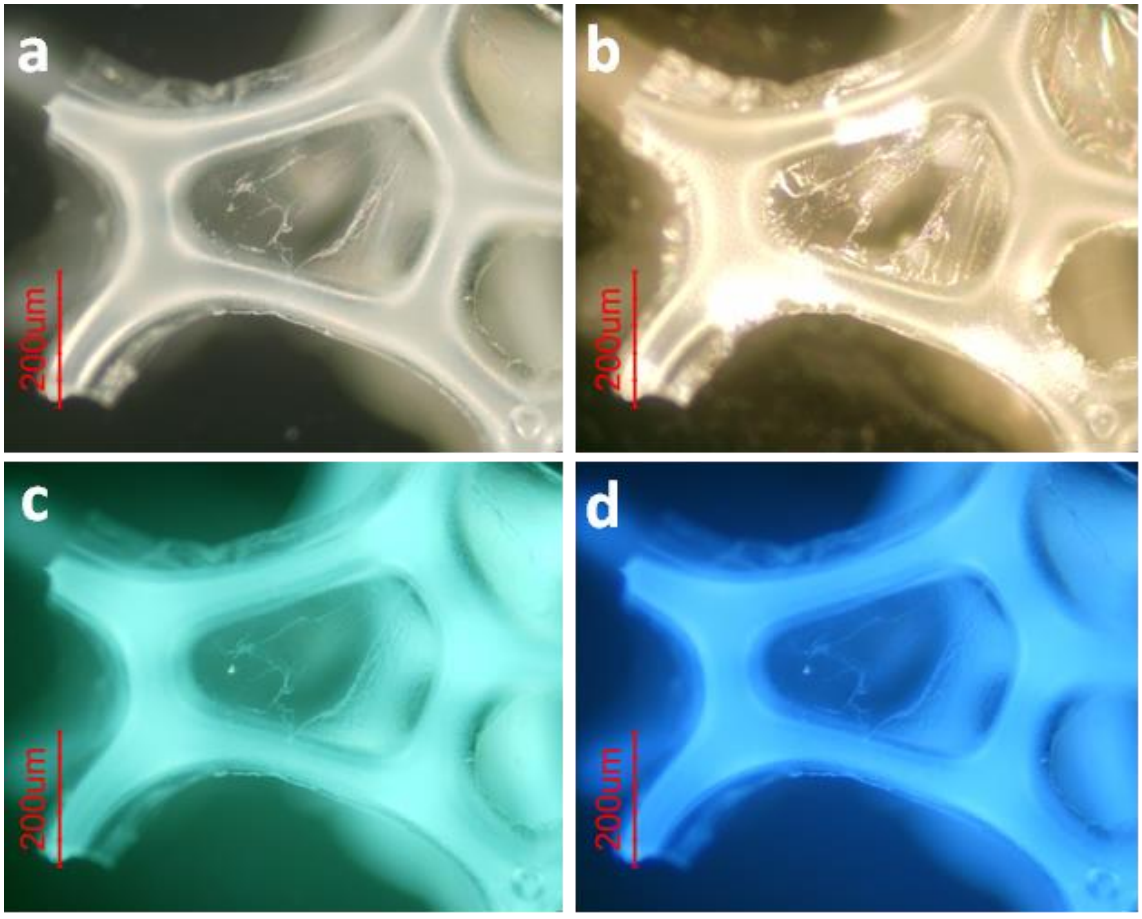


Figure 3.13 Microscopy images of the model PUR moulded foam cell bun under reflected cross-polarised light (a), darkfield (b), blue-violet light (c) and ultraviolet light (d).

The moulded foam is not transparent, its colour is light beige, and the fluorescence intensity is also stronger (Fig. 3.1 compared to 3.13c,d). As explained by the foam supplier, this might be justified by the use of liquid MDI (darker) instead of liquid TDI (transparent, or pale shade). In addition, MDI has two aromatic rings, while TDI has only one (see Chapter 1). Consequently, the TDI/MDI blend results in foams with longer systems of conjugated double bonds which at the end, possibly justifies the light beige colour and the higher intensity levels of fluorescence under the same wavelengths.

From infrared spectroscopy, the model spectrum (black) shows the characteristic bands of ether-based PUR moulded foams (Fig. 3.14)[71] (Dounis & Wilkes, 1997; Kaushiva & Wilkes, 2000).

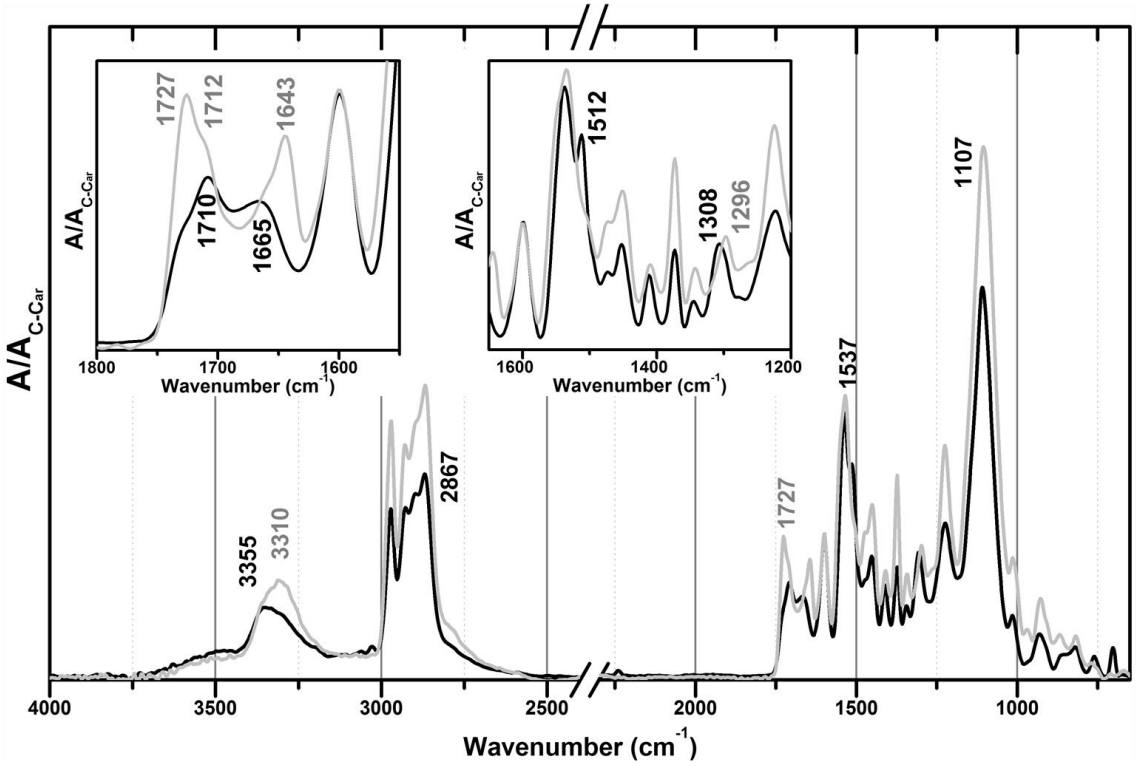


Figure 3.14 Infrared spectra of model ether-based PUR foams: cold-moulded (black) and slabstock (grey). Insets: detail of the C=O stretching region from 1800 to 1550 cm^{-1} (left) and detail of C–N stretching absorptions at 1512 and c. 1300 cm^{-1} (right).

In the same figure, a comparison between moulded and slabstock spectra is shown (Fig. 3.14). The absorption bands between 3500–3200 cm^{-1} (N–H stretching) and 1750–1600 cm^{-1} (C=O stretching) are the most altered, shifting to different frequencies. As supported by the literature, this indicates the use of reactive polyols and crosslinking agents, which consequently, result in short and less ordered

[71] See Appendix IV for a complete assignment of IR bands.

Figure 3.15 Polyether-based PUR moulded foam case studies from the MUDE collection. From top to bottom: *Cactus*, Egg, Pratone and *Capitello*. Photos: ©MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

HS domains in PUR moulded foams (Dounis & Wilkes, 1997; Kaushiva & Wilkes, 2000). Since the N–H stretching maximum shifts from c. 3310 cm^{-1} (slabstock) to c. 3355 cm^{-1} (moulded), i.e., to higher frequencies (decrease of H-bonded N–H groups), longer lengths could be assumed to be present between HS chains from the hard domain. Regarding the carbonyl region, while bidentate urea (c. 1643 cm^{-1}) appears in slabstock foams, monodentate urea (c. 1665 cm^{-1}) and free urea/loosely associated urethane (1710 cm^{-1}) appear in the moulded foam spectrum (Dounis & Wilkes, 1997; Li *et al*., 2002). Furthermore, the presence of TDI/MDI blends may be confirmed by the appearance of an absorption band at 1512 cm^{-1} (C–N stretching and N–H bending of amide II) and shift of the 1296 band to 1308 cm^{-1} (C–N stretching). Consequently, infrared markers for the distinction of slabstock and cold-moulded ether-based PUR foams are proposed. If absorptions at c. 1660 cm^{-1} (instead of a band at c. 1640 cm^{-1}), c. 1535 and c. 1512 cm^{-1} (instead of one single band at c. 1535 cm^{-1}), and c. 1310 cm^{-1} (instead of a band at 1296 cm^{-1}) are shown, there is a high probability of being a cold-moulded PUR foam (based on TDI/MDI blends). However, careful analysis should be carried out since deteriorated slabstock foams show similar changes on the carbonyl region, as previously discussed.

3.3.2.2 Historical ether-based PUR cold-moulded foams

For this section, four case studies from the MUDE collection (designed between 1968 and 1972) were selected (Fig. 3.15). In this set, all foams were likely produced from TDI/MDI blends and ether-based polyols. The collected foams from *Egg*, *Cactus* and *Pratone* are examples of fair condition (physical stability when handled, elasticity of the cell net); while the collected foam from *Capitello* represents an unacceptable condition (fragile network and complete loss of elasticity).

However, in this study, establishing a deterioration course based on the exclusive analysis of these historical objects' foams was more difficult since a non-clear correlation (in some cases) between the image of the PUR cell buns and the IR spectra was observed. This hindrance could be

related to the presence of relatively different foam formulations between the model and the case studies. For example, while IR spectroscopy indicated similar compositions between them (Fig. 3.16) (as well as the previously proposed infrared markers of a TDI/MDI blend in all case studies), optical microscopy revealed significant colour differences (Fig. 3.17).

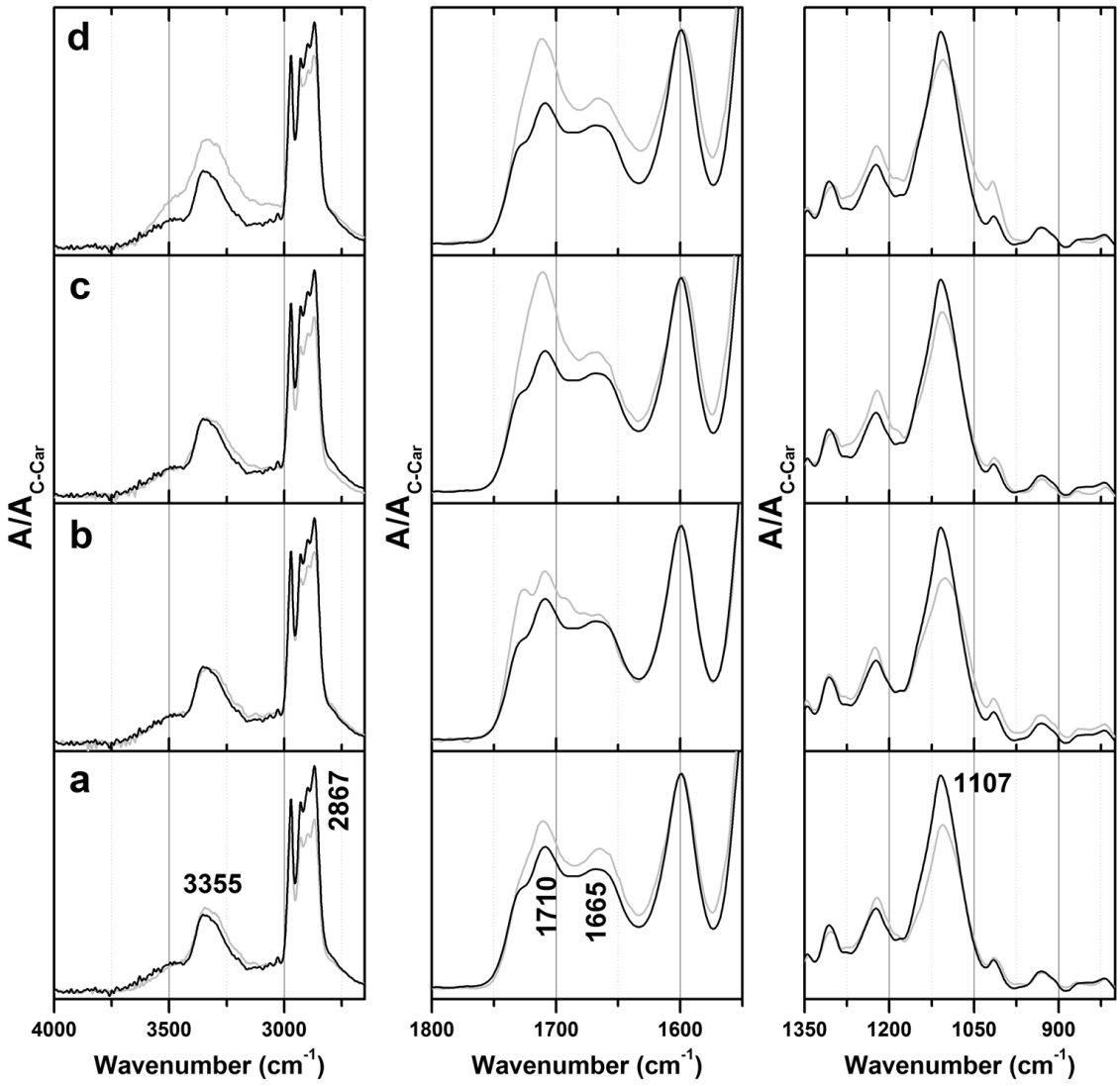


Figure 3.16 Infrared spectra of the unaged model PUR cold-moulded foam (black) and the PUR foams from the cold-moulded case studies from the MUDE collection (grey) showing different condition grades: N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). Fair condition grade: *Cactus* (a), *Egg* (b) and *Pratone* (c). Unacceptable condition grade: *Capitello* (d).

Whereas the cell buns from the case studies are transparent (Fig. 3.17), the cell buns from the model are white/beige (Fig. 3.13), and this gain in transparency cannot be attributed to ageing. According to the model supplier, this colour variation might be justified by a different proportion of the TDI/MDI blend right at t=0, which in turn, was not detected by IR spectroscopy.

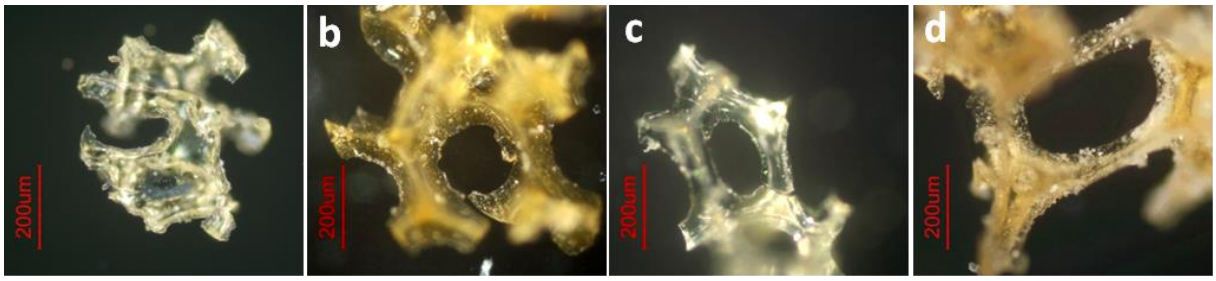


Figure 3.17 Microscopy images under reflected cross-polarised light of the PUR foam cell buns collected from cold-moulded case studies from the MUDE collection showing different condition grades. Fair condition grade: *Cactus* (a), *Egg* (b) and *Pratone* (c). Unacceptable condition grade: *Capitello* (d).

Aside from this, additional data hindered the correlation between the IR spectra and the visual image of the PUR foams from the case studies. Foams showing clear signs of ageing under the microscope (such as yellowing and micro holes) (Fig. 3.17) have resulted in infrared spectra showing mostly minor/small changes in bands relative intensities (Fig. 3.16b). Also, while the foam from *Pratone* (Fig. 3.17c) apparently shows (based on OM) a better condition than the foam from *Egg* (Fig. 3.17b), their infrared spectra point to different conclusions, i.e. less spectral changes are detected in the *Egg*'s foam (Fig. 3.16b) than in the *Pratone*'s foam (Fig. 3.16c). This is especially observed in the carbonyl region, which has been assigned as an important spectral region to detect deterioration in PUR (Gardette & Lemaire, 1981; Wilhelm & Gardette, 1998). Aside from these observations, two additional hypotheses were posed: (i) the presence of different foam formulations within the case studies and (ii) the presence of complex stratigraphies which resulted in different exposure degrees of the foams to deterioration agents. Regarding the first hypothesis (i), although *Cactus*, *Pratone* and *Capitello* were produced by the same firm (Gufram) and in the same period (designed in 1971 and 1972, and probably produced in 1986 as indicated by the firm label signature in the objects[72]); Izzo *et al.* identified different foam formulations (by SEM-EDS, FTIR-ATR and Py-Gc-MS) in different *Pratone* seats[73] from 1986[74] (Izzo *et al*., 2015). According to her, although the three *Pratone* belong to the Gufram Multipli' 86 series, the last object (94/200) showed a different foam formulation. For that reason, different formulations could be present among *Cactus*, *Pratone* and *Capitello*. Regarding the second reason (ii), all these PUR cold-moulded foams are highly covered by other layers and show complex stratigraphies[75] (Fig. 3.18), which could have influenced their condition until today.

[72] See Appendix III for more details.
[73] In Izzo *et al*.'s study, the materials used to produce *Pratone* 12/200, 24/200 and 94/200 were compared. In this investigation, *Pratone* 17/200 is studied.
[74] This highlights the experimentalism character of design firms such as Gufram, in Italy.
[75] It was not possible to have the standard cross-section preparation in polyester resin due to damages to the morphology caused during polishing.

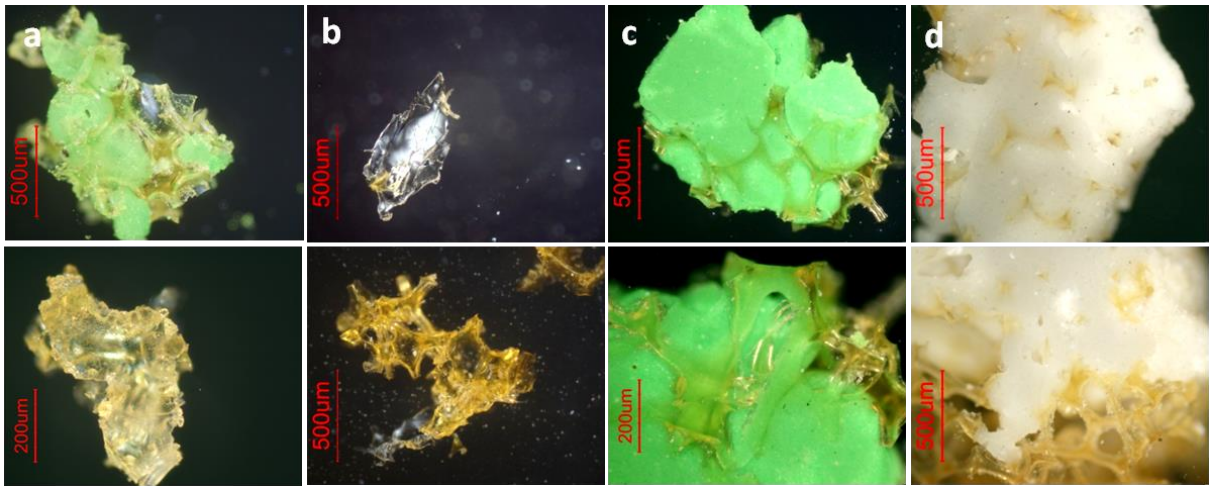


Figure 3.18 Microscopy images under reflected cross-polarised light of coating layers/integral skins above the PUR cold-moulded foam from the selected objects from the MUDE collection. From top to bottom: *Cactus* green polyisoprene coating and intermediate layer (a), *Egg* PVC integral skin and foam (b), *Pratone* green polyisoprene coating and foam (c) and *Capitello* white polyisoprene coating and foam (d).

As confirmed by IR analysis (see Appendix V), the foams from *Cactus*, *Pratone* and *Capitello* are covered by thick paint layers of coloured poly(isoprene) (green or white), while the foam collected from the *Egg* shows an integral skin made of PVC. In addition, *Cactus* shows an extra layer possibly made of a blend of poly(chloroprene) and a phenolic resin. As a result, the foam from *Cactus* shows definitely the highest protection barrier from external deterioration agents (two layers), whereas the collected foams from *Pratone* and *Capitello* show the lowest protection degree – *Pratone* because the foam sampling was carried out in a fracture area (rupture of the grass arm at the bottom), and *Capitello* because sampling was carried out in an open hole found at the base (see Appendix V). Regarding *Egg*, in addition to the protection offered by the green fabric (Fig. 3.15) and the PVC integral skin (Fig. 3.18b), the chair has been stored in its closed position (see Appendix III), which decreases the interaction of light and oxygen.

Consequently, the deterioration course of PUR cold-moulded foams was not possible to suggest based on the exclusive interpretation of the present case studies.

To overcome this poor correlation, two extra case studies were added, namely, *Viúva Negra* (1981) and *Nova Olímpia* (1981), both sculptures by João Vieira (1934–2009) (see Appendix III). These artworks are made of ether-based PUR cold-moulded foams, show fair (*Nova Olímpia*), poor and unacceptable conditions (*Viúva Negra*) (Fig. 3.19) and were produced at the same firm as the model. Due to the absence of paint layers or PVC integral skins, the relationship between PUR cell buns visual

aspect and infrared spectra was easier to assess, making these artworks valuable sources for the present study.

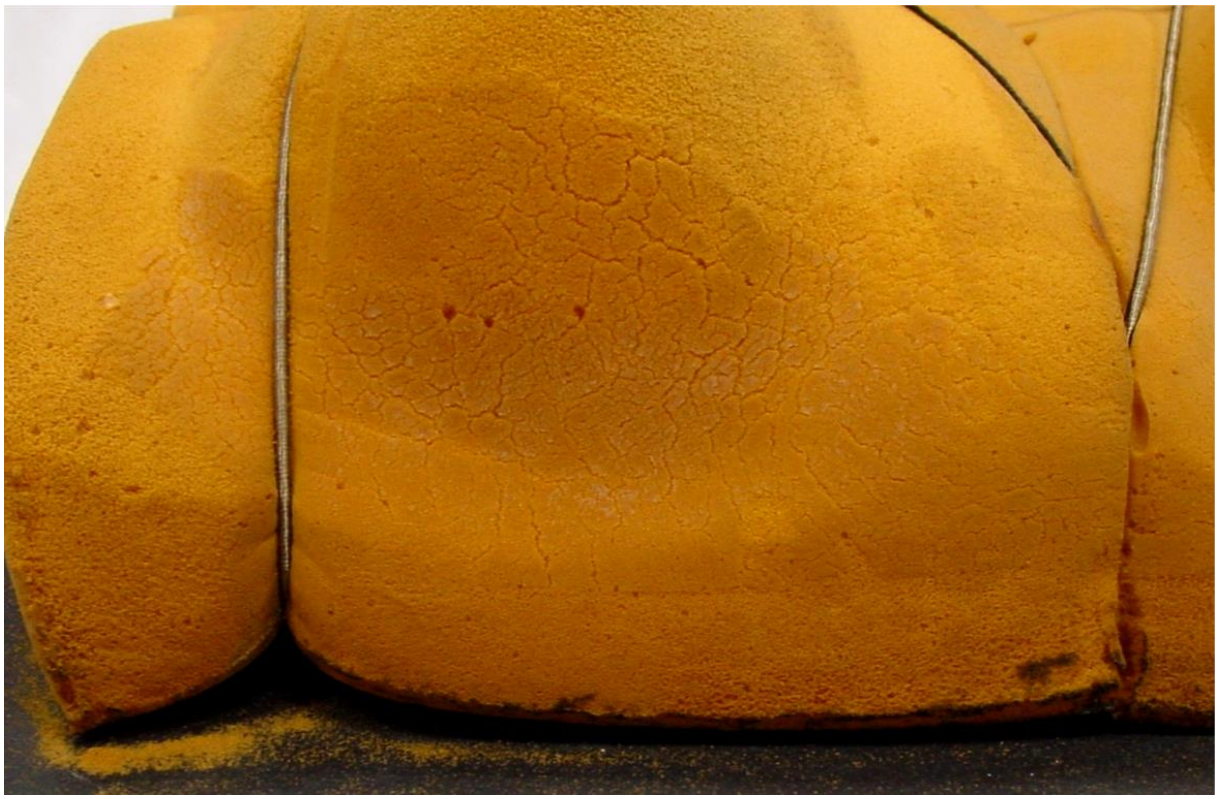


Figure 3.19 João Vieira, *Viúva Negra*, 1981. Detail of the PUR cold-moulded foam showing an unacceptable condition: yellowing and crumbling (polyurethane foam powders and loss of material).

The presence of different conditions is related to the artworks biographies: whereas *Nova Olímpia* has been kept for the last ten years inside a plastic bag; *Viúva Negra* has been hanged on a wall, next to a window, at least since the late 1980s. As a result, the foam from *Nova Olímpia* shows good elasticity when handled, while the foam from *Viúva Negra* shows diverse conditions – fair (areas more protected from light), poor (areas which show a fragile network, prone to crumbling when handled) and unacceptable (powdered PUR and areas of skin cracking). Figure 3.20 shows the OM images of the collected PUR foam cell buns from both artworks. From these images, different conditions are observed (Fig. 3.13 compared to 3.20) and the visual ageing progress of ether-based PUR cold-moulded foams could be proposed. In general, the ageing course may be detected by the increase of yellowing (Fig. 3.20, under cross-polarised light), loss of shine (Fig. 3.20, under darkfield light), formation of defects at the surface of the cells struts and ultimately, on the complete collapse of the foam (Fig. 3.20e).

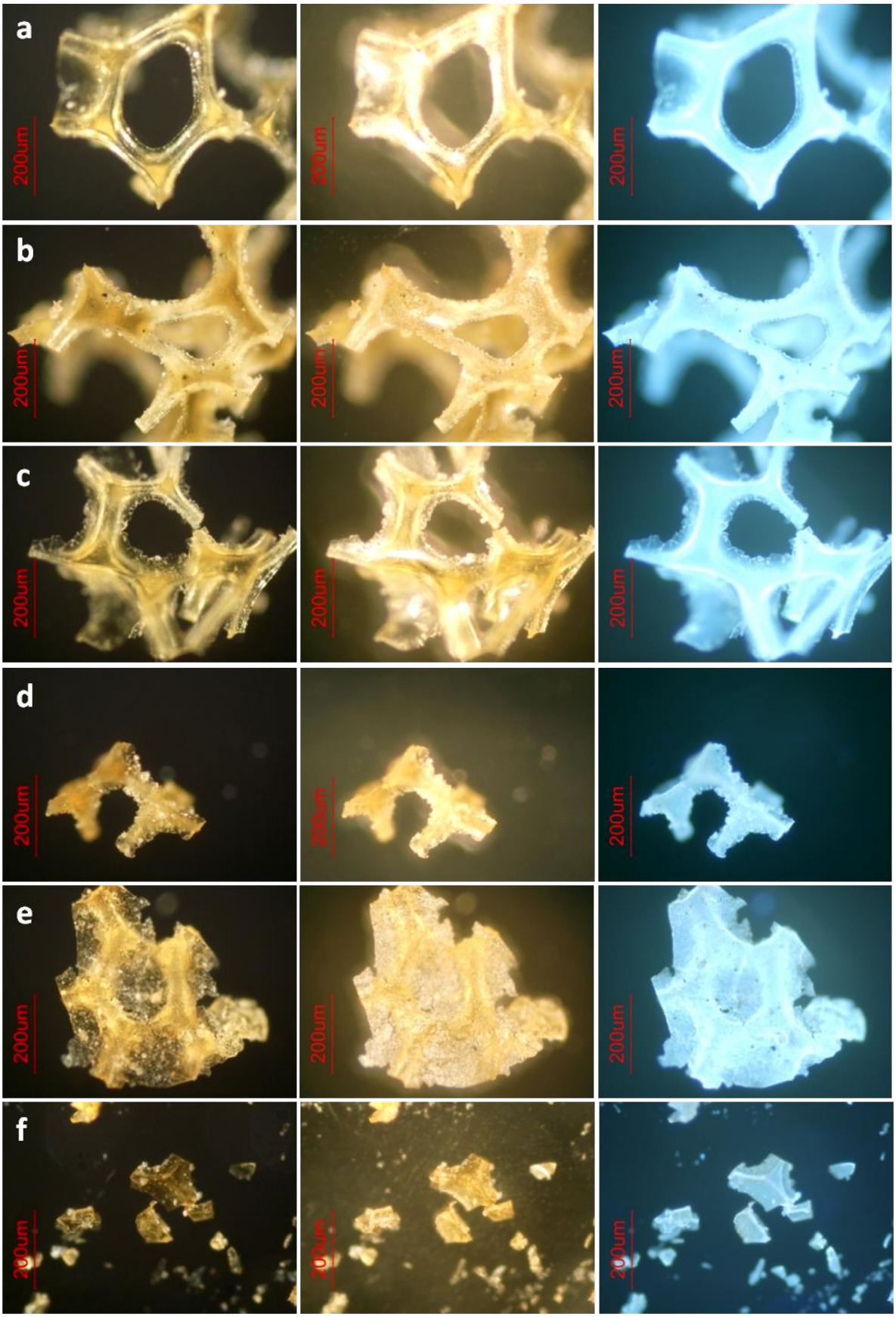


Figure 3.20 Microscopy images of PUR cold-moulded foam cell buns collected from *Nova Olímpia* (a,b) and *Viúva Negra* (c–f) showing different condition grades. From left to right: under reflected cross-polarised light, darkfield and ultraviolet light. Fair condition (a–c), poor condition (d) and unacceptable condition (e,f).

The formation of defects such as outline disruptions and micro holes is associated to fair conditions (Fig. 3.20a–c), while the formation of micro cracks, fractures and pitting (in a smaller scale) is associated to poor and unacceptable conditions (Fig. 3.20d–f). As expected, this shows similarities with the ageing of PUR slabstock foams (Figs. 3.5 and 3.6).

On the other hand, the IR spectroscopy results of PUR cold-moulded foams (Fig. 3.21) and slabstock foams (Fig. 3.7) points to significant differences between the two ageing progresses. Although once more the N–H, C–H and C=O stretching regions are the most affected, the N–H and C=O stretching regions show relevant differences. While fair and poor slabstock foam spectra do not show clearly visible changes in the N–H stretching region (3730–3160 cm^{-1}), cold-moulded foam spectra show (in general) variations right at these grades (Fig. 3.7 compared to Figs. 3.16 and 3.21). This might suggest that the system of H-bonds in moulded foams is more susceptible to deterioration than in slabstock foams. As discussed in Chapter 1, PUR moulded foams show weakly ordered HS domains (reflected by the presence of monodentate urea) as consequence of weaker H-bonds between HS chains (Dounis & Wilkes, 1997; Zhang *et al*., 1998). Furthermore, not only Moreland *et al*. believed that the presence of humidity replaces some H-bonds for water molecules (promoting localized chain slippage) (Moreland *et al*., 1994a, 1994b), as Dounis and Wilkes stated that high 'humidities 'plasticized' the moulded foams to a greater extent than the slabstock foams' (Dounis & Wilkes, 1997: 2819). Taking these statements into account and the results from the previous section (3.3.1), the higher susceptibility of H-bonds in moulded foams to deterioration might be confirmed. As shown in Fig. 3.21., the monodentate urea band (c. 1665 cm^{-1}) shifted to bidentate urea (c. 1643 cm^{-1}) (Fig. 3.21a,b) right at fair conditions, and the high increase of the resulting band (at 1640 cm^{-1}) was never observed. This evidence could point to the higher weakness of H-bonds interactions in moulded foams, when compared to slabstock foams (Dounis & Wilkes, 1997), and consequently, to the increase disorder of the HS domain during ageing. Along with the spectral changes detected in the carbonyl region, the N–H absorptions also show a shift from 3355 to 3282 cm^{-1} (Fig. 3.21a), and to 3300 cm^{-1} (Fig. 3.21b), indicating the formation of new H-bonded species. Further ageing also suggests the complete disarrangement of the hard domain. There is an increase of the bands at c. 1708 and c. 1727 cm^{-1}, indicating the decrease (at c. 1708 cm^{-1}) or the complete loss (at c. 1727 cm^{-1}) of H-bonds in urea and urethane linkages.

As these conclusions are proposed from the condition assessment of historical objects, ageing experiments on model samples were carried out to verify the results.

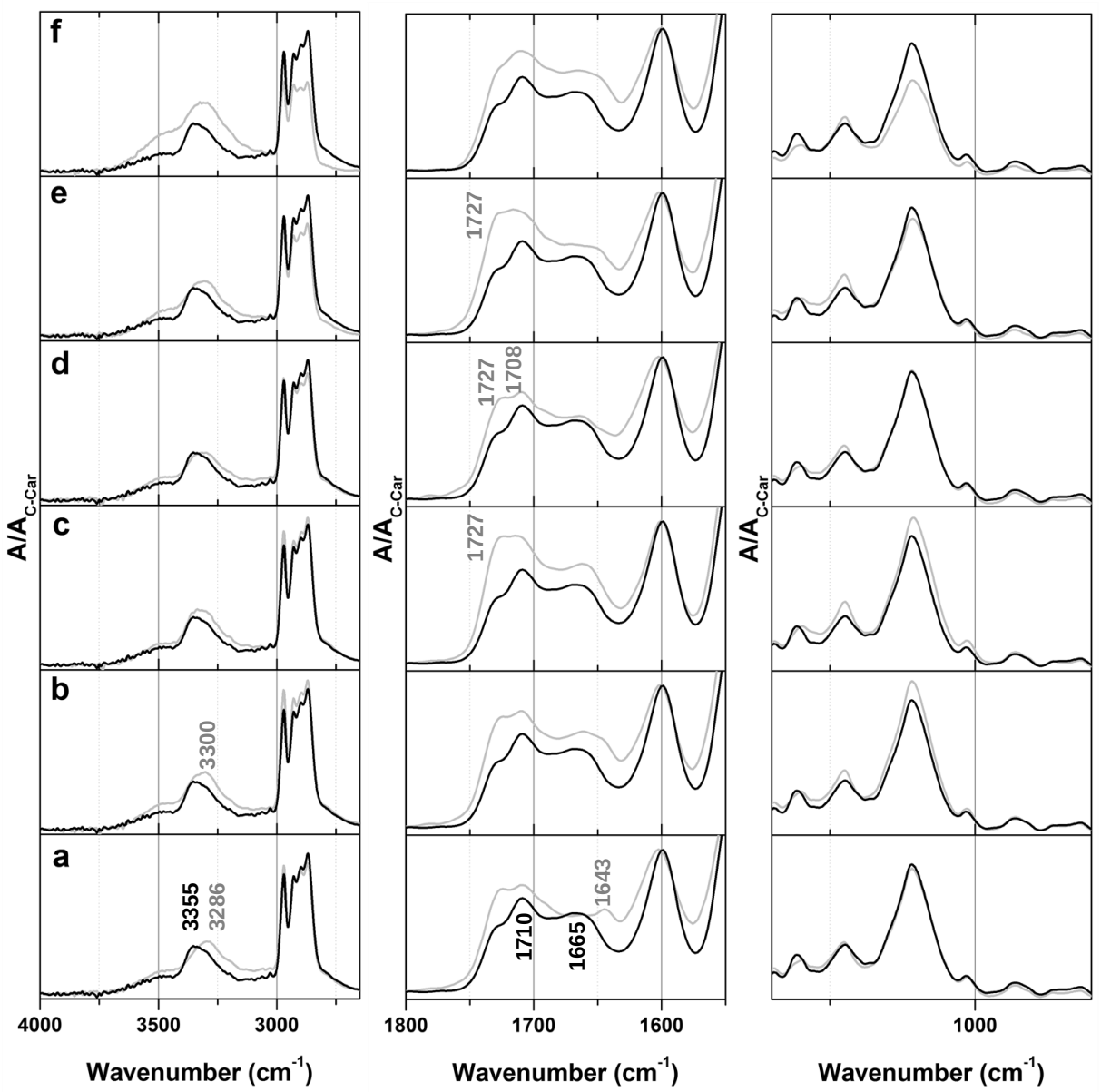


Figure 3.21 Infrared spectra of the unaged model PUR cold-moulded foam (black) and the PUR foams from *Nova Olímpia* (a,b) and *Viúva Negra* (c-f) (grey) showing different condition grades: N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). Fair condition grade: *Nova Olímpia* (a,b) and *Viúva Negra* (c). Poor condition grade: *Viúva Negra* (d). Unacceptable condition grade: *Viúva Negra* (e,f).

3.3.2.3 Ageing experiments for the model sample

For the validation of the previously suggested deterioration course, the model PUR cold-moulded foam was submitted to the same ageing conditions as the slabstock model. Since the outdoor ageing showed more comparable results with the case studies (in comparison with the artificial light ageing), only the

outdoor ageing is discussed[76]. The visual ageing progress is shown in Fig. 3.22. As observed, the damages are similar to the ones found on the historical foams.

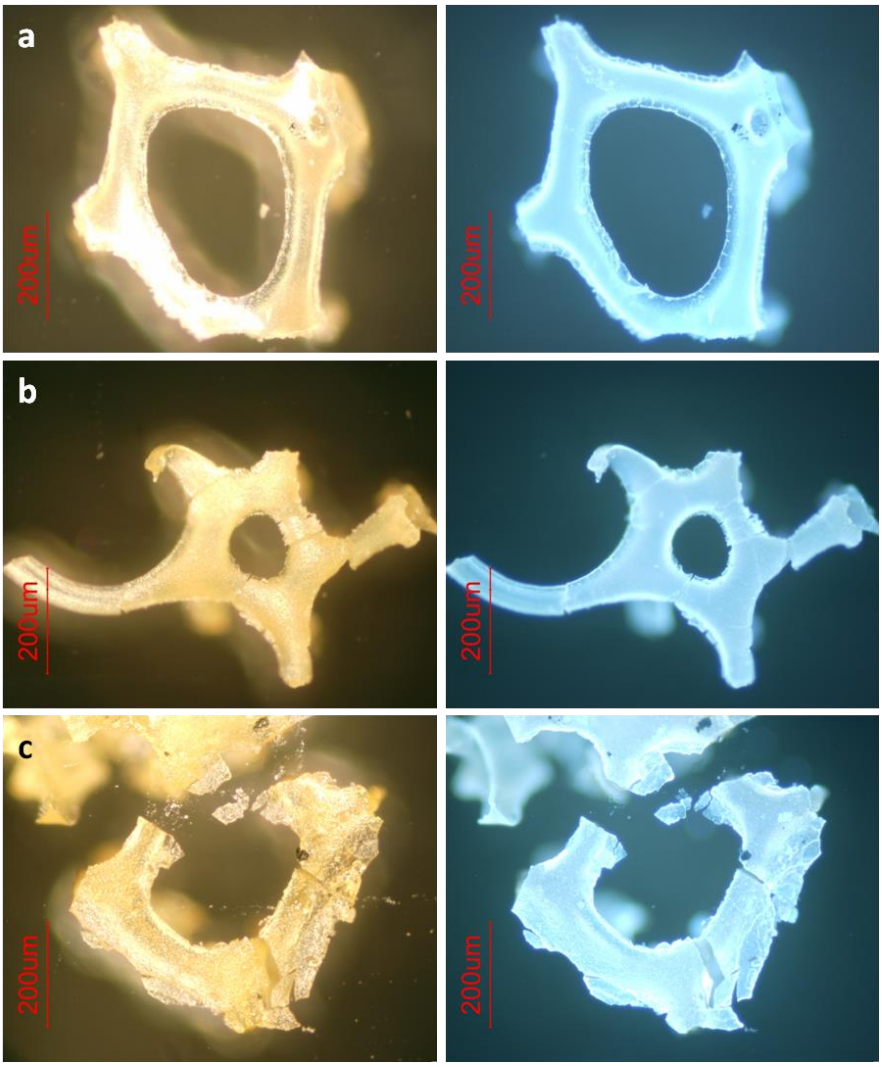


Figure 3.22 Microscopy images of the model PUR cold-moulded foam cell bun after one and a half (a) three (b) and five (c) months of natural (outdoor) ageing under darkfield (left) and ultraviolet light (right).

Yellowing and disruptions of the outline shape of the cell strut are observed after one and a half months of ageing (Fig. 3.22a), while the formation of cracks and fractures completely crossing the cell struts are detected after three months (Fig. 3.22b) and more severely observed after five months (Fig.

[76] In both models of PUR slabstock and moulded foams, the artificial light ageing (UV-Vis λ> 300nm) led to a high increase of both O–H/N–H and C=O relative intensities between 3600–3150 cm^{-1} and at c. 1725 cm^{-1}, respectively, right at early stages of ageing (e.g. only after 2 days of exposure). However, this extent of deterioration was never detected on PUR foam-based objects from the MUDE collection. For that reason, in general, the outdoor ageing resulted in closer results to the case studies than the artificial light ageing. This might be related to the continuous presence of intense light during the entire artificial ageing and to the extreme photochemical sensitivity of the soft segment (ether-based), which leads to the formation of hydroperoxides, formates (main photoproduct), esters, hemiacetals, alcohols and carboxylic acids in a high extent (Gardette & Lemaire, 1981; Wilhelm & Gardette, 1998).

3.22c). Contrary to what was previously mentioned (aged slabstock model), these fractures are clearly visible in the aged model and therefore, are not a deterioration sign correlated to handling. This fact, once more, may indicate the HS domain in moulded foams as more prone to ageing than slabstock foams (under the same ageing conditions), as supported by the literature.

From the infrared results (Fig. 3.23), although the model ageing progress shows similarities with the historical foams, the shift of monodentate urea to bidentate urea was not observed. Therefore, this shift could be associated to former deterioration stages (that could have been present before the first sampling at t=1.5 months) or to the effect of specific ageing conditions that were not present in this ageing experiment. Still, the N–H, C=O and C–O–C stretching regions show the same deterioration tendency as the case studies. From unaged to aged conditions, PUR moulded foams show the increase of N–H relative intensities between 3600–3200 cm^{-1} (along with a slight shift to lower frequencies), the decrease of C–H relative intensities, the increase of C=O stretching bands at c. 1710 cm^{-1} (at first) and then at c. 1720 cm^{-1} (increase of C=O groups, free or loosely associated through H-bonds), and the decrease of the C–O–C stretching relative intensity at c. 1100 cm^{-1}.

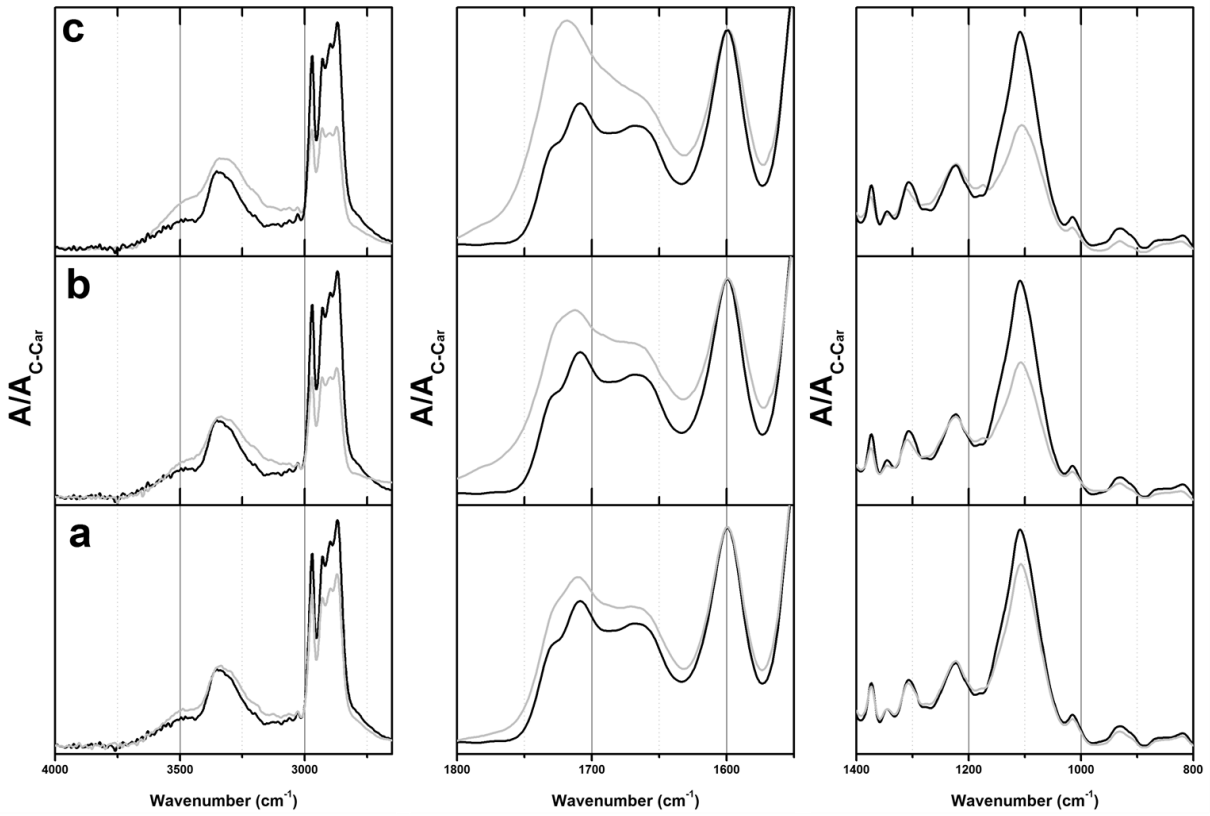


Figure 3.23 Infrared spectra of the model PUR cold-moulded foam before (black) and after (grey) natural ageing (outdoor): N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). After one and a half (a), three (b) and five months (c).

In comparison with PUR slabstock foams, the ageing of PUR cold-moulded foams results (in general) in the continuous relative intensity increase of the C=O band at c. 1660 cm^{-1} (along with a slight shift to 1675 cm^{-1}), following to the possible overlapping of this band by the appearance of a C=O band at c. 1720 cm^{-1}. Moreover, the formation of a band at c. 1640 cm^{-1} during ageing, as found in some aged slabstock foams (both references and case studies) was not observed. Therefore, urea groups in PUR cold-moulded foams do not show the same tendency (as in slabstock foams) to establish strong hydrogen-bonding interactions during ageing (with water molecules or other radicals formed). This, in turn, may result in completely different ageing behaviours of these foams, which lead to even less packed HS domains (during ageing), in a morphology with less elasticity and finally, in the formation of cracks crossing the entire cell struts (as found in Fig. 3.22b,c). Corroborating this was the higher tendency to crumble (when handled) observed in samples collected from PUR cold-moulded foams, while PUR slabstock foams showed a slight degree of viscosity.
Overall, PUR cold-moulded foams show different ageing behaviours than PUR slabstock foams, under the same ageing conditions.

The following section intends to compare the deterioration behaviour of ether- and ester-based slabstock foams. Although it is known that ester-based PUR foams are more prone to hydrolysis than ether-based PUR foams, in this research, the visual and molecular ageing course of the two PUR foam types is compared under the presence of light and relationships with historical case studies are established.

3.4. Ester-based PUR flexible foams

3.4.1. Ester-based PUR slabstock foams

3.4.1.1 Model sample of ester-based PUR slabstock foam

Based on optical microscopy, the visual description of the unaged ester- and ether-based cell buns from PUR slabstock foams is similar: bright whitish colour, absence of defects at the surface of the cell struts and clean lines (Fig. 3.24a,b). Under blue-violet and ultraviolet light, comparable fluorescence behaviours are also detected (Fig. 3.24c,d). Consequently, it is proven that the presence of a different polyol class (ester-based, instead of ether-based) does not change the fluorescence behaviour of these foams, corroborating the previously mentioned hypothesis for the fluorescence of these foams (presence of aromatic and amide molecular structures on the polyurethane backbone).

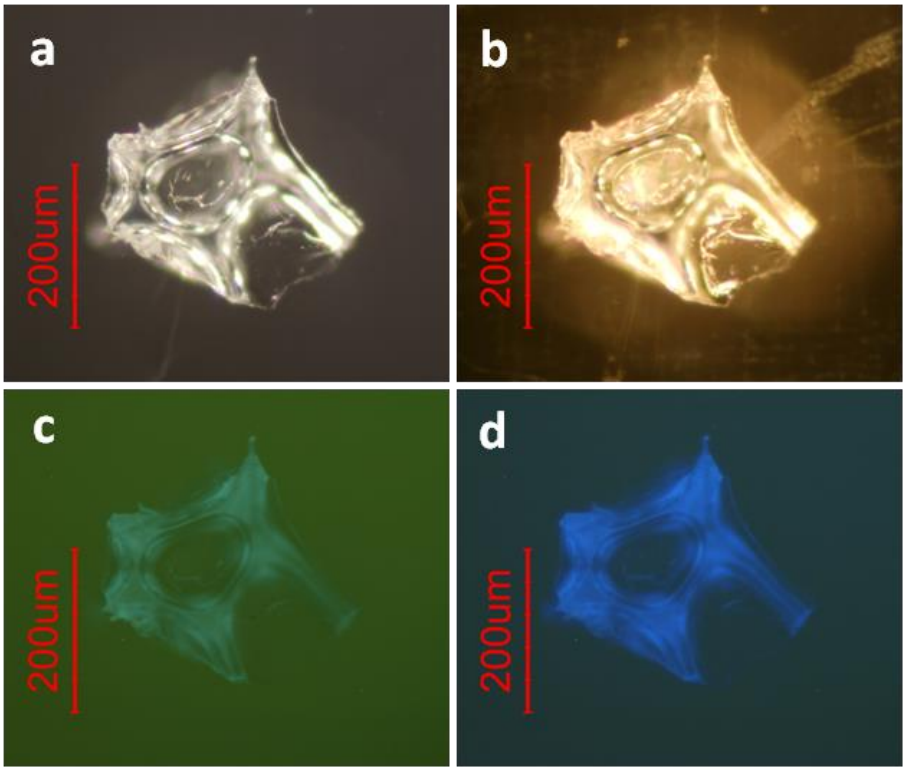


Figure 3.24 Microscopy images of the model PUR slabstock foam cell bun under reflected cross-polarised light (a), darkfield (b), blue-violet light (c) and ultraviolet light (d).

From infrared spectroscopy, a typical formulation of ester-based PUR slabstock foam was detected[77] (Pellizzi *et al*., 2014, 2016; Lattuati-Derieux *et al*., 2011; Lovett & Eastop, 2004). As shown in Fig. 3.25, instead of the strong band at 1107 cm^{-1} (assigned to C–O–C stretching and consequently, to ether-based PUR), ester-based PUR show the characteristic bands of ester-based SS: strong C=O stretching band at 1734 cm^{-1} and lower C–O–C stretching bands between 1230–1000 cm^{-1}. As supported by the literature, these bands can be used to distinguish between ether- and ester-based PUR flexible foams (Lattuati-Derieux *et al*., 2011). In the C–H stretching region (3000–2800 cm^{-1}), spectral differences are also recorded. Instead of the complex band profile (four main maxima) shown by typical ether-based PUR slabstock foams, this model only shows two main maxima, as observed in other studies (Lattuati-Derieux *et al*., 2011; Pellizzi *et al*., 2016). This could be related to the absence of $C–H_3$ groups in the molecular structure of the ester-based segment. The remaining assignment is similar to the ether-based slabstock model. Regarding hydrogen-bonding interactions, the presence of non-associated (free) C=O is confirmed by the stretching band at 1734 cm^{-1} and the presence of strongly associated C=O by the stretching band at 1643 cm^{-1} (Priester *et al*., 1990; Elwell *et al*., 1996). Although the band

[77] See Appendix IV for a complete assignment of IR bands.

at 1734 cm^{-1} is assigned to C=O groups from the SS, this band is also masking the C=O groups from the urethane linkage, which would be detected at c. 1727 cm^{-1}. Nevertheless, both frequencies are acquainted to C=O absorptions free of H-bonds. Concerning the N–H stretching region, at c. 3530 cm^{-1} is the free N–H and at c. 3320 cm^{-1} the H-bonded N-H stretching. Once more, this foam shows an ordered HS domain, as typically found on PUR slabstock foams (Priester *et al*., 1990).

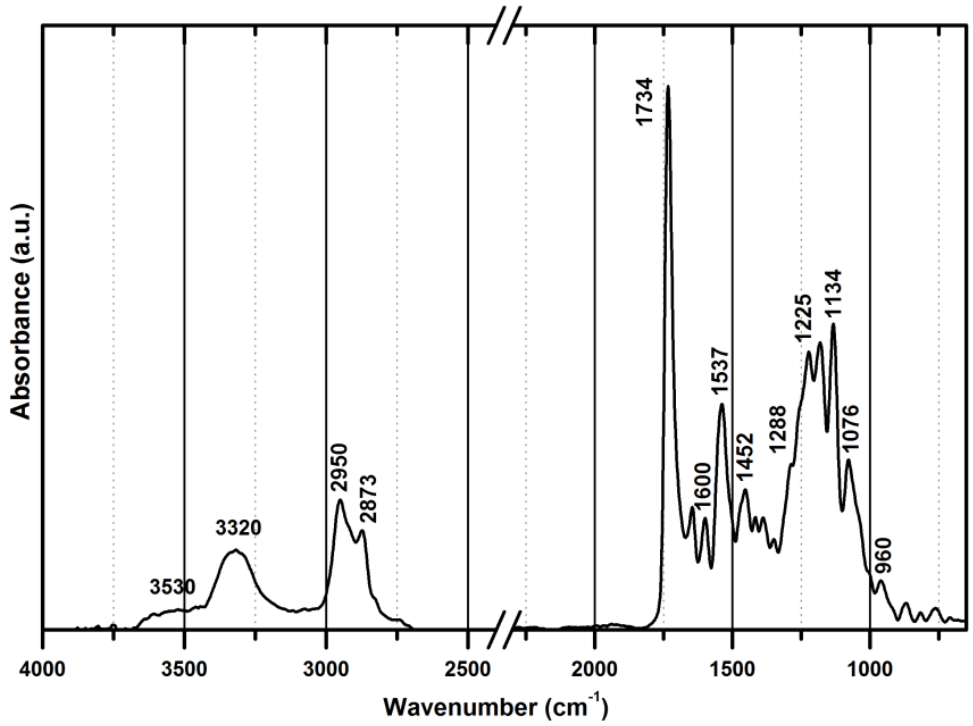


Figure 3.25 Infrared spectrum of the model ester-based PUR slabstock foam.

3.4.1.2 Historical ester-based PUR slabstock foams

For this study, only two objects were found in the MUDE collection[78]. Nevertheless, only one (aluminium foil jacket filled with PUR foam[79]) was selected since the two objects showed different foam processes: slabstock (foam from the jacket) and quasi collapse (foam from a standing lamp[80]). To compare this section with section 3.3.1.1, only the slabstock case is discussed, and more PUR-based objects were added. Unfortunately, apart from one single case showing a fair condition (particularly requested to a foam supplier), all cases found show unacceptable conditions (high discolouration,

[78] Since ester-based polyols for PUR foams started to be left aside during the 1970s (due to poor resistance to hydrolysis) and most of the MUDE collection is dated from 1960s onwards, this situation was not unexpected.
[79] Although in the beginning of this research this case study was part of Francisco Capelo collection (deposited in MUDE), the object was offered by the owner to the author of this dissertation for research purposes.
[80] See Appendix III for more information on the object.

complete collapse of the cell net, viscous residue when handled and/or presence of white powders in the cell net): foam from the metal foil jacket (1960s) (Fig. 3.26), foam from the padding of a turntable needle (1980s) (Fig. 3.27) and foam from the seating cushions of a car (1994) (Fig. 3.28). The whole set is likely to be made of TDI and ester-based polyols based on adipic acid-diethylene glycol polyester, as indicated by IR spectroscopy.

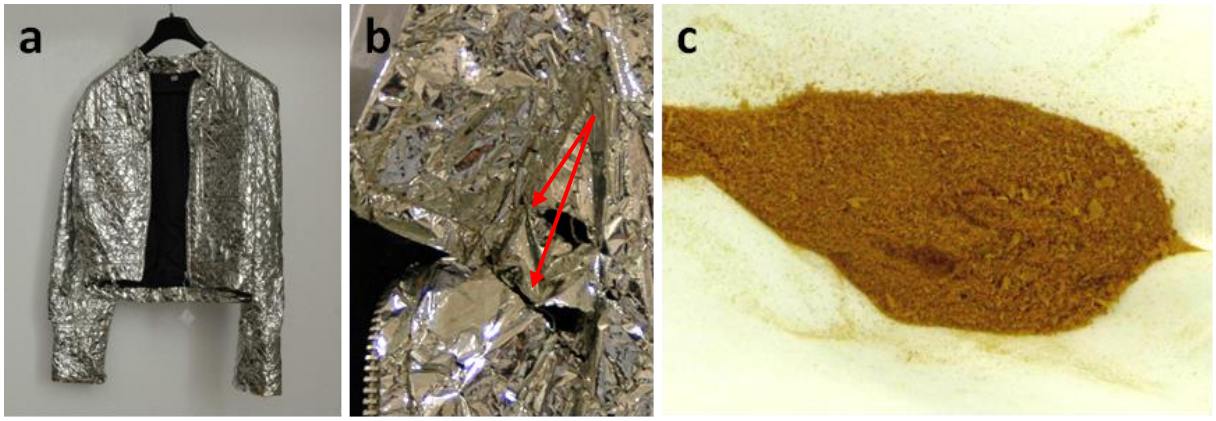


Figure 3.26 Unknown author, jacket, c. 1960s: general view (a), metal foil tears (the arrows indicate tears) (b) and collapsed polyurethane deposited in the protective cover (c).

Figure 3.27 Detail of ester-based PUR foam condition from the padding of the turntable needle: yellowing and crumbling.

Figure 3.28 Detail of the ester-based PUR slabstock foam from the seating cushions of a car (1994) showing an unacceptable condition: intense yellowing (brown colour) and crumbling.

Based on optical microscopy, the visual aspects related to these foams ageing processes are shown (Fig. 3.29). Discolouration (into yellow, orange or brown colours) (Fig. 3.29b–d), presence of fractures crossing the entire cell struts (Fig. 3.29c,d) and formation of adipic acid (white crystals) (Fig. 3.29c,d) are the main visual signs associated to ageing. By comparing these samples with the ether-based slabstock foams, significant differences were detected. Whereas ether-based showed (in general) a tendency to crumble when handled and a slight tackiness (leaving a transparent residue during manipulation), the foams from Fig. 3.29b,c are highly viscous, sticky and form clumps with minor manipulation. The foam from Fig. 3.29d, also showed a viscous behaviour, although smaller. In addition, poor and unacceptable ether-based PUR slabstock foams clearly show the formation of defects at the surface of the cell struts (disruptions of the cell edge lines, holes, micro cracks and pitting - causing a high diffraction of light under darkfield microscopy), whereas the historical ester-based foams do not show this type of defects, even in extreme deteriorated cases. Instead, clean and bright surfaces are observed (Fig. 3.29b,c), especially up to the spread formation of adipic acid, which masks the clean surface (Fig. 3.29d).

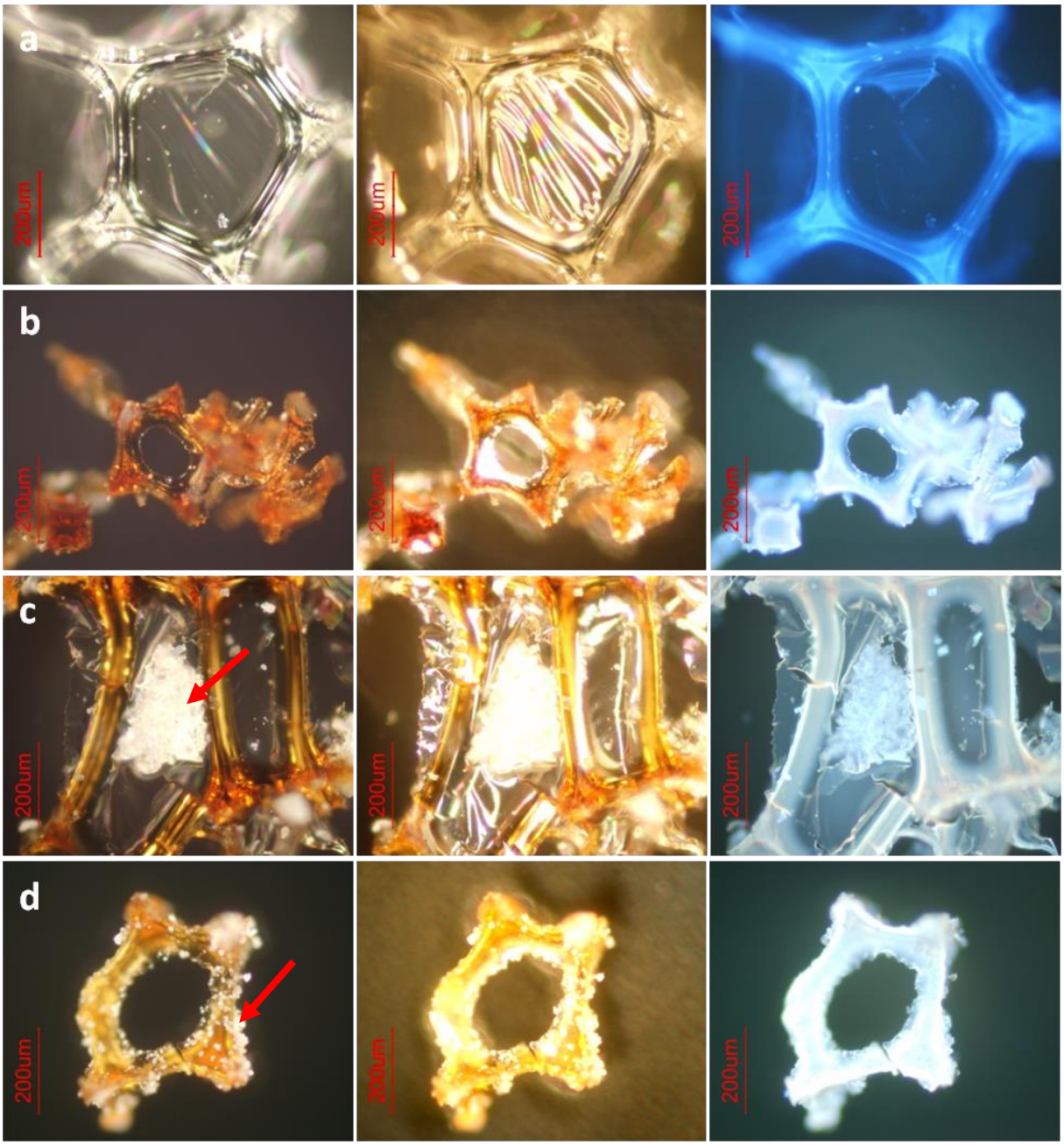


Figure 3.29 Microscopy images of ester-based PUR slabstock foam cell buns collected from historical objects showing different condition grades. From left to right: under reflected cross-polarised light, darkfield and ultraviolet light. Fair condition grade: foam from c. 2006 (a). Unacceptable condition grade: foam from 1994, collected from car cushions (b), foam from 1980s, collected from the padding of a needle turntable (c), and foam from 1960s, collected from the filling of a metal foil jacket (d). The arrows indicate the presence of adipic acid (white crystals) and fractures.

Based on infrared spectroscopy, these visual changes (related to ageing) were translated into new spectral lines and the molecular ageing course of these foams was suggested (Fig. 3.30). As shown, fair conditions may be associated to the decrease of C=O and C–O–C stretching bands relative intensity

(Fig. 3.30). As supported by the literature, this change could be related to the deterioration of ester-based SS by hydrolysis (Pellizzi *et al*., 2014).

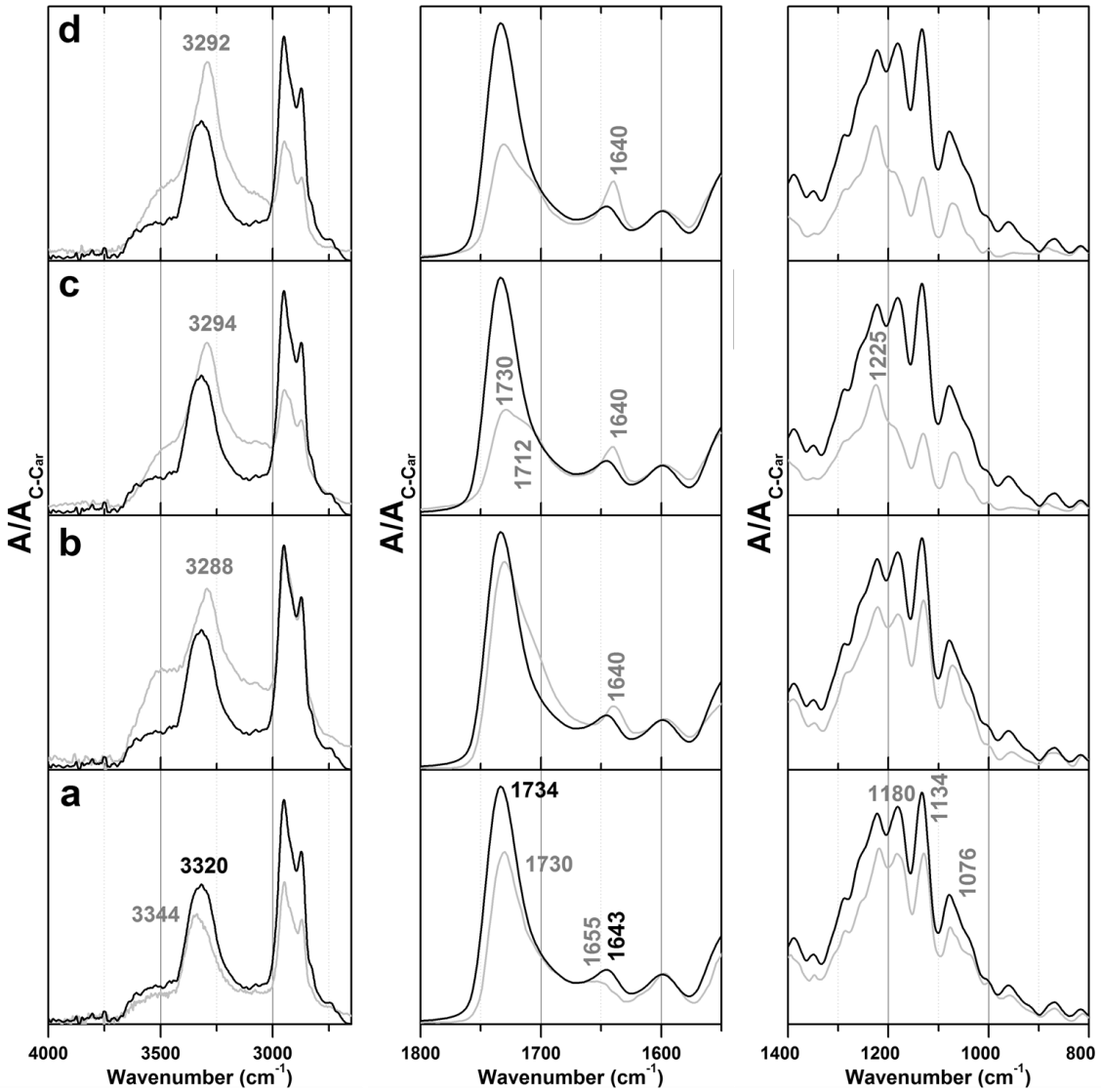


Figure 3.30 Infrared spectra of the unaged model PUR slabstock foam (black) and the PUR foams from the case studies (grey) showing different condition grades: N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). Fair condition grade: foam from c. 2006 (a). Unacceptable condition grade: foam from 1994, collected from car cushions (b), foam from 1980s, collected from the padding of a needle turntable (c), and foam from 1960s, collected from the filling of a metal foil jacket (d).

Significant shifts in the N–H and C=O stretching regions are also observed at this stage of ageing. Along with the C=O shift from 1643 cm^{-1} (strong H-bonded urea) to 1655 cm^{-1}, the N–H band shifts from 3320 cm^{-1} to higher frequencies, 3344 cm^{-1}. Consequently, the loss of H-bonds between urea linkages from the HS domain in ester-based PUR slabstock foams is also observed and ester-based foams showing fair conditions could have suffered a disarrangement (disordering) in the HS domain, as well

as the hydrolysis of ester bonds from the SS domain. Further ageing stages (in this case, exclusively unacceptable conditions) are probably associated to the plasticisation phenomenon of HS chains by water molecules, as stated by Moreland *et al.* for an ether-based PUR foam, and Boubakri *et al.,* for an ester-based TPU (Moreland *et al*., 1994a, 1994b; Boubakri *et al.,* 2009). This may be clearly visible in the infrared spectra through the appearance and increase of the band relative intensity at c. 1640 cm^{-1} (Fig. 3.30b–d), as observed in ether-based PUR foams. Along with this spectral change, the shift of the N–H stretching band from 3320 cm^{-1} to lower frequencies is detected, also suggesting the increase of H-bonded N–H species. Regarding the C=O stretching band at 1734 cm^{-1}, although the broadening of this band is observed in Fig. 3.29b, the high decrease in its relative intensity is detected in Fig. 3.30c,d, suggesting that acid species are being formed within the polymer network (as consequence of ester groups hydrolysis), up to the clear precipitation of white crystals (confirmed as adipic acid[81] by IR spectroscopy, Fig. 3.31) among the cell net.

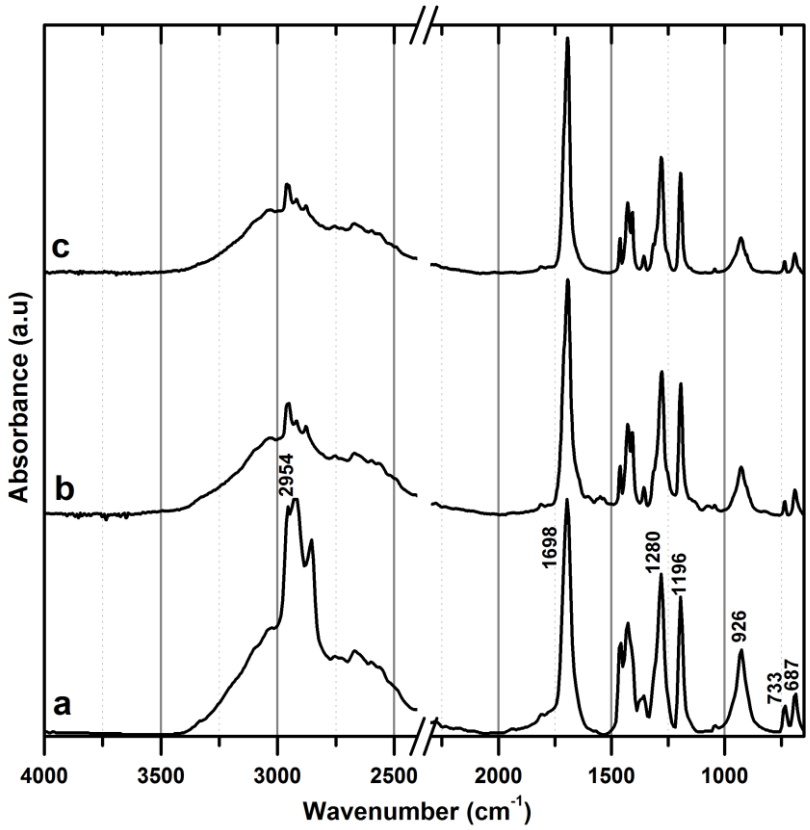


Figure 3.31 Infrared spectra of adipic acid 99+% reference (a) and the white crystals collected from the case studies (b,c): from the foam padding of a needle turntable (b) and from the foam filling of the metal foil jacket (c).

[81] The infrared spectrum of adipic acid, 99+% was obtained from the Aldrich Condensed Phase Library database, Index 3931, CAS 124-04-9. The spectra in this library are published in *The Aldrich Library of FT-IR Spectra*, vols. 1 and 2. Adipic acid shows a broad band between 3300–2500 (O–H stretching), three stronger bands between 2950–2855 (C–H stretching) and an intense and characteristic band at c. 1700 (C=O stretching) (Ren *et al*., 2009; Brioude *et al*., 2007).

As stated in the literature, the band at c. 1712 cm^{-1} 'is indicative of the presence of un-reacted –COOH' (Pavia *et al*., 1996 and Nakanishi & Soloman, 1977 as cited in Brioude *et al*., 2007: 336) and 'the intensity of this band increases proportionally to the adipic acid content in the polymer' (Brioude *et al*., 2007: 336). Consequently, it may be suggested that the formation of adipic acid could be associated to the saturation of the acid content in the polymer, causing its precipitation as white crystals. Corroborating this hypothesis is the decrease of the C=O stretching band at 1734 cm^{-1} (as consequence of ester hydrolysis and acid formation) and the decrease of the band between 3750–3350 cm^{-1} from Fig. 3.30b to Fig. 3.30c,d, which may indicate the decrease of the OH content in the polymer, as consequence of acid precipitation.

Similarly to the methodology presented on section 3.2, the model was submitted to natural (outdoor) and artificial (UV-Vis radiation, λ > 300nm) ageing in order to validate the previous results. Yet, the discussion is limited to the natural (outdoor) ageing results since the selected artificial ageing conditions (photo) led to ageing behaviours more distant from the historical foams. This situation was not unexpected since ester-based PUR foams are more prone to hydrolysis than to photo-ageing. Although an artificial ageing experiment could have been carried out in humid atmosphere, this was already executed by the Popart Project research group (90°C and <10% RH, compared to 90°C and 50% RH) and discussed in detail in the literature (Pellizzi *et al*., 2014). From the Pellizzi *et al.* study, the decrease of the band at 1727 cm^{-1} was observed, along with the appearance of a band at 1690 cm^{-1} and increase of the band at 1640 cm^{-1}. Even though they attributed the decrease at 1727 cm^{-1} to the hydrolysis of the SS domain, and the appearance of the band at 1690 cm^{-1} to the formation of adipic acid, nothing was mentioned in relation to the increase of the band at 1640 cm^{-1}. Therefore, the carrying out of the natural ageing in outdoor conditions was selected to include the influence of light and to avoid artificial conditions. In this case, although the outdoor ageing time was extended up to six months, no adipic acid was formed.

3.4.1.3 Ageing experiments for the model sample

Based on optical microscopy, similar visual decay with the PUR foams from the historical objects was observed on the aged model under outdoor conditions (Fig. 3.32). Yellowing and loss of transparency were clearly observed after one and a half months of ageing, increasing in intensity up to six months, and when handled, a high level of viscosity was observed after three months of ageing, also increasing up to the six months. As shown in Fig. 3.32, the formation of imperfections at the surface of the cell struts was not observed, remaining clean and shiny, even when extremely degraded as observed after 6 months of ageing. A justification for the superior gain in viscosity (during ageing) of ester-based PUR

foams when compared to ether-based (under the same ageing conditions) might be related to different water diffusion coefficients. As known, the presence of the carbonyl group in ester-based SS (absent in ether-based SS) results in higher water diffusion.

Comparably to the unaged sample, the fluorescence intensity of the aged samples is higher, as consequence of the probable formation of oxidised species and new conjugated double bonds during ageing (as previously explained).

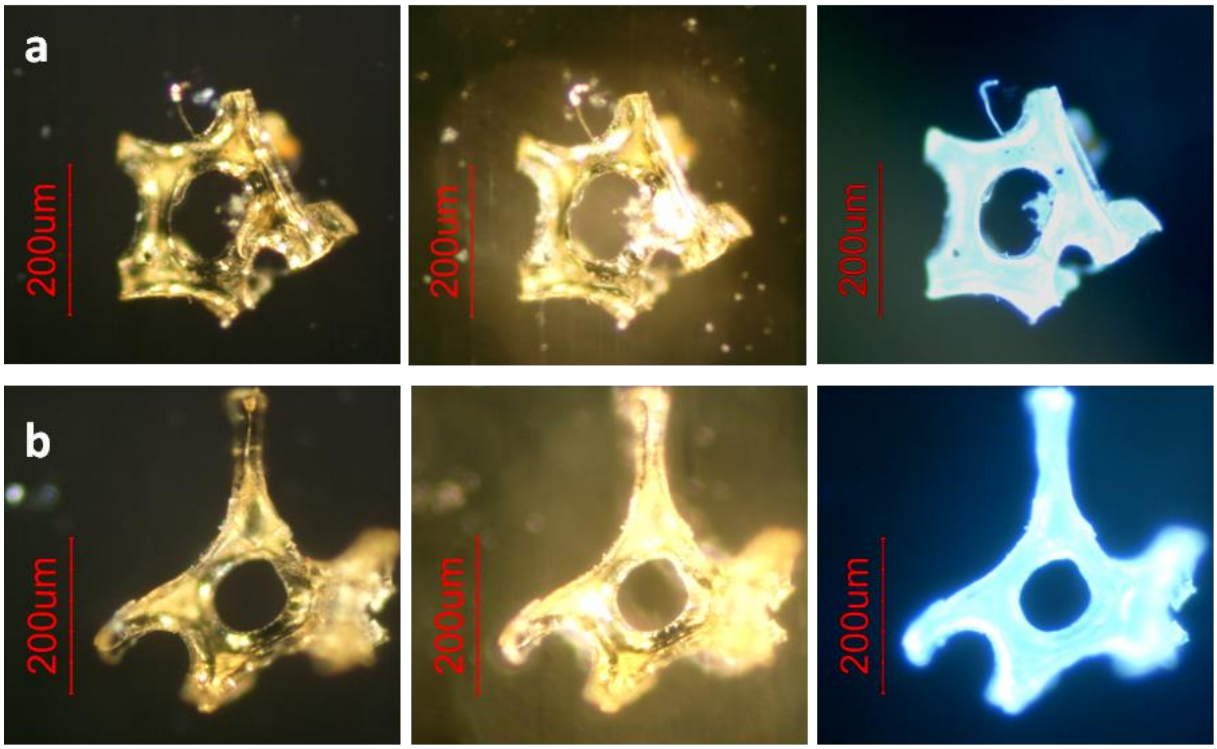


Figure 3.32 Microscopy images of the model PUR slasbtock foam cell bun after three (a) and six (c) months of natural (outdoor) ageing under reflected cross-polarised (left), darkfield (centre) and ultraviolet light (right).

From infrared spectroscopy (Fig. 3.33), although some similarities with the historical foams spectra were found, it may be possible to conclude that the presence of light (during the outdoor ageing) has resulted in the increase of the C=O stretching band at 1730 cm^{-1} during the first stages of ageing. On the other hand, since fluctuating RH and T were also present (in the outdoor ageing), comparable spectral changes with the case studies were also recorded.

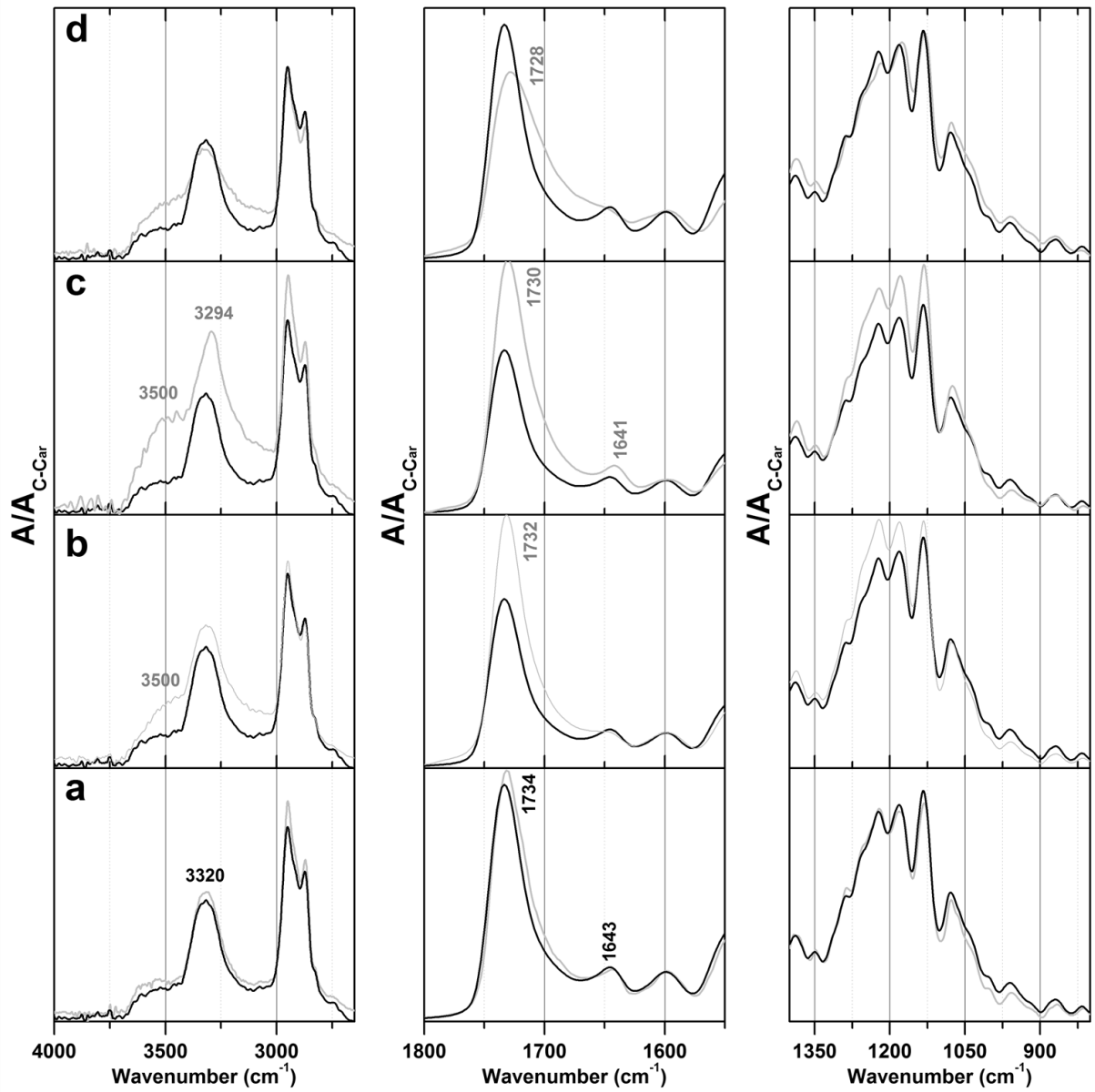


Figure 3.33 Infrared spectra of the model PUR slabstock foam before (black) and after (grey) natural ageing (outdoor): N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). After one and a half (a), three (b) five (c) and six months (d).

In relation to the N-H stretching region, the increase of the bands relative intensity is observed, along with the shift of the band at 3320 to c. 3294 cm^{-1}. In the C=O stretching region, the shift of the band at 1734 to c. 1728 cm^{-1} was also observed, followed by the increase of the band at c. 1640 cm^{-1}. These spectral changes may indicate the increase of hydrogen-bonding interactions in urea linkages (plasticisation phenomenon of the HS chains by water molecules) and the hydrolysis of ester groups from the SS. Still, it was confirmed that the presence of light induces different degradation courses in this type of foams (since the increase of the C=O stretching band at c. 1730 cm^{-1} was also detected during the artificial light ageing). As consequence, light should also be considered as a harmful

deterioration agent for ester-based PUR foams and taken into consideration for the decision making-process involved, for example, in the definition of display periods for museum objects containing ester-based PUR foams.

Since the MUDE collection also includes objects showing ester-based TPU films and coatings, and these materials have been poorly focused on conservation studies, the following section intends to expand the current knowledge about their deterioration.

3.5. Ester based TPU films

3.5.1 Ester-based TPU coatings in artificial leathers

3.5.1 Model sample of ester-based TPU film

Although the selected case studies consist on TPU artificial leathers based on complex stratigraphies of (i) urethane-based top coating, (ii) adhesive layer and (iii) textile support; for this discussion, only the top layer is being considered and therefore, the model was produced to fulfil this demand. The model is composed by pure *Estane® 5708 F4,* an ester-based TPU film. Consequently, the possible influence of adhesives and textile supports was not studied.

The visual characteristics of the unaged model (thin films of *Estane® 5708 F4*) can be described from their observation under the microscope, Fig. 3.34. The images show the film surface. As observed, the model is characterised by flat and bright surfaces (Fig. 3.34a), which show fluorescence under blue-violet (strong) and ultraviolet (weak) lights (Fig. 3.34b,c). The molecular groups most likely responsible for this fluorescence were already discussed in previous sections of this chapter.

Based on infrared spectroscopy (Fig. 3.35), the model shows common infrared absorptions for ester-based TPU films[82] (Wilhelm & Gardette, 1997 and citations therein; Srichatrapimuk & Cooper, 1978 as cited in Marsh & Schoonover, 1998; Schoonover *et al*., 2001). The soft-segment is characterised by the C=O stretching band centred at 1732 cm^{-1}, the C–O–C stretching bands at 1255 and 1173 cm^{-1} and the C–H_2 stretching bands between 3000–2800 cm^{-1}. The band centred at 1732 cm^{-1} overlaps with infrared absorptions related to the HS domain. As shown in Fig. 3.35 (inset), this band is a complex mixture of

[82] See Appendix IV for a complete assignment of IR bands.

several absorptions which masks absorptions related to different hydrogen-bonding interactions in urethane linkages. The remaining bands of the spectrum have already been assigned in previous sections.

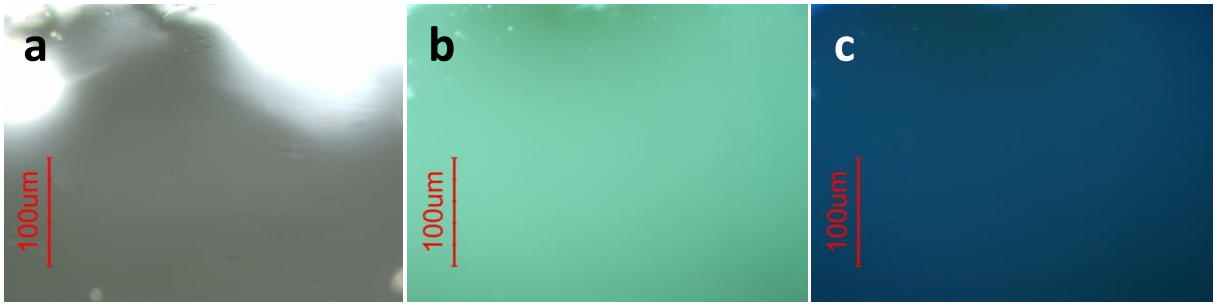


Figure 3.34 Microscopy images of the model TPU film surface under reflected cross-polarised light (a), blue-violet light (b) and ultraviolet light (c).

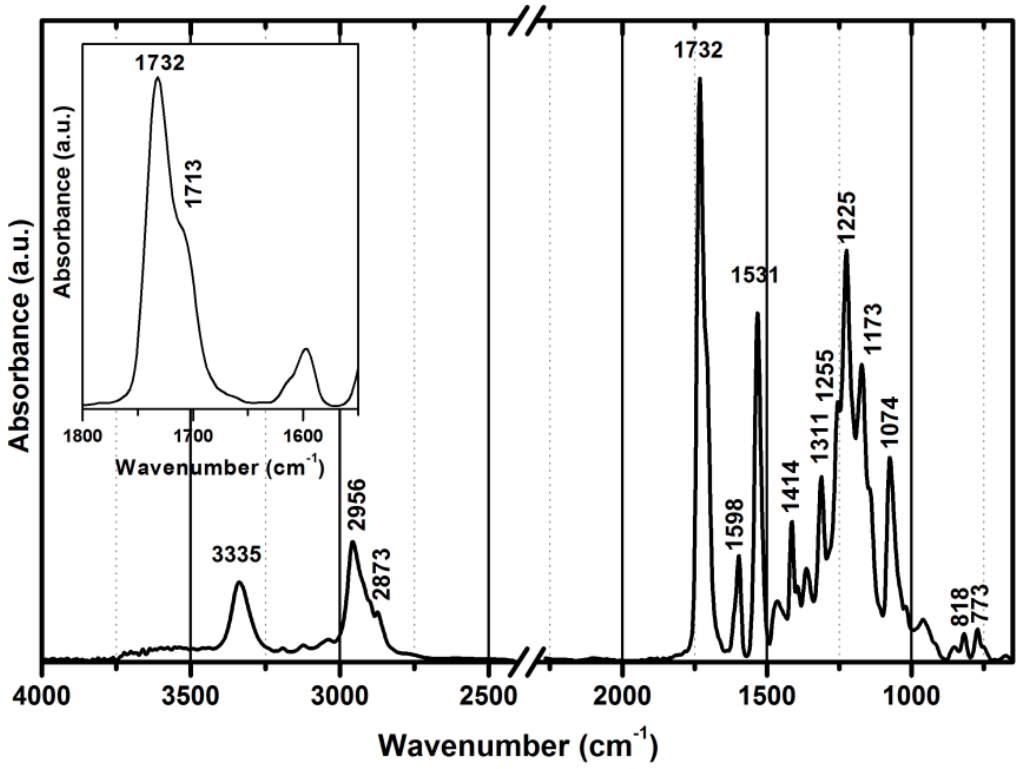


Figure 3.35 Infrared spectrum of the model TPU film. Inset: Detail of the carbonyl region from 1800 to 1550 cm^{-1}.

Regarding the hydrogen-bonding interactions, the presence of associated (H-bonded) urethane is confirmed by the absorption bands at 3335 cm^{-1} (N–H stretching) and 1713 cm^{-1} (C=O stretching), which, in turn, confirm the existence of an ordered HS domain (Wang & Cooper, 1983; Li *et al*., 1992 and Sui *et al*., 2015 as cited in Tian *et al*., 2015: 1756).

3.5.2 Historical ester-based TPU coatings in artificial leathers

From the study of five TPU (thermoplastic urethane elastomer) films/coatings from design and fashion objects from the MUDE collection (based on MDI and ester-based polyols), three case studies dated between the late 1960s and early 1970s are discussed in this section, as they summarise the results obtained from the extended set.

The selected set is composed of fashion garments created by the French designer André Courrèges (1923–2016) with artificial leathers (Fig. 3.36)[83] showing several conditions: the artificial leather from the brown dress (1970) is an example of fair condition (shiny and physically stable when handled); the less degraded areas from the artificial leathers of both the blue dress (c. 1965) and the blue long jacket (c. 1971) represent poor conditions (dull appearance of the leather); and the most degraded areas from both these objects are examples of unacceptable conditions (high level of fragility when handled and clear presence of white powders on the surface) (Figs. 3.37 and 3.38).

Figure 3.36 Ester-based TPU coating case studies from the MUDE collection. From left to right: André Courrèges, brown dress (1970), André Courrèges, blue dress (c. 1965) and André Courrèges, blue long jacket (c. 1971). Photos: ©MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

[83] See Appendix III for enlarged images and more details about the objects.

Figure 3.37 Detail of the ester-based TPU coating case studies condition in 2012. (a) André Courrèges, brown dress (1970), (b) André Courrèges, blue dress (c. 1965), and (c) André Courrèges, blue long jacket (c. 1971).

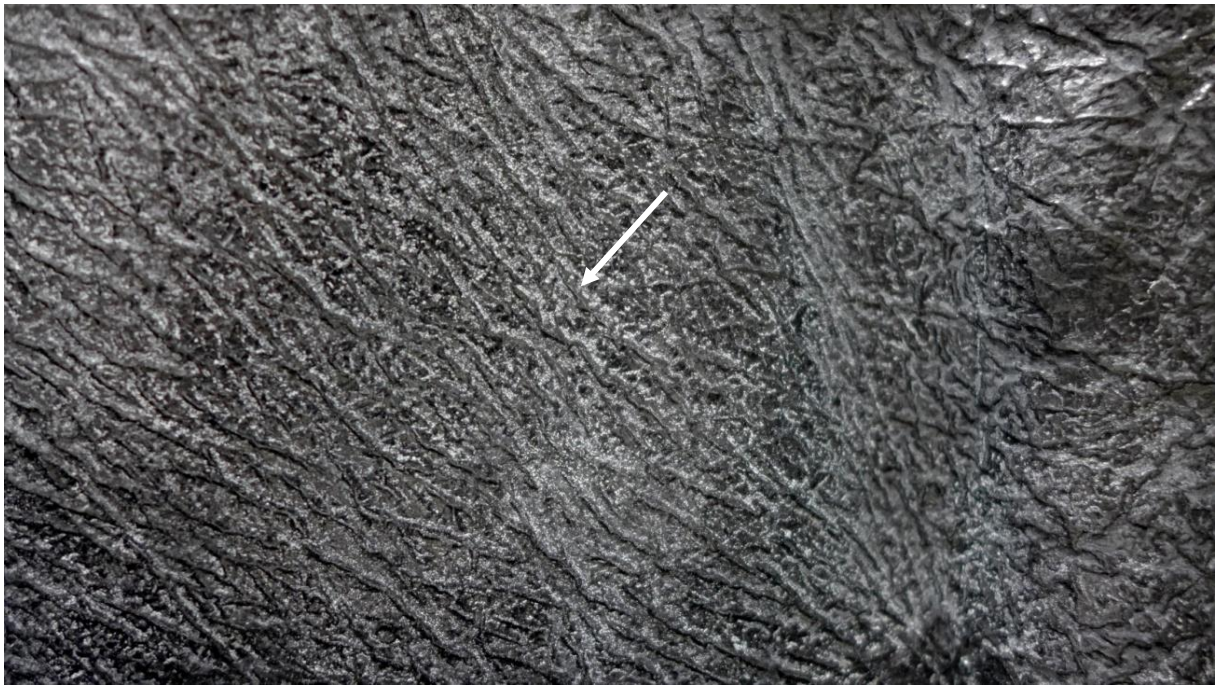


Figure 3.38 André Courrèges, blue long jacket, c. 1971. Detail of its highly deteriorated artificial leather based on TPU, showing white powders on its surface (the arrows indicate the white products among the leather texture).

As shown in Fig. 3.37, the brown artificial leather delimiting the cut and shape of the brown dress remains lustrous, undamaged and flexible (Fig. 3.37a), whereas the blue artificial leathers from the last two cases are tarnished, dull, show white powders at the surface, and are highly fragile when handled (Fig. 3.37b,c).

Since these pieces have close production dates (1965–1971) and their incorporation into the museum happened at the same time (2002), once more, biography (such as wearing frequency), composition of the TPUs formulation (influence of colourants and/or additives) and/or manufacturing processes could be the reason for their different condition in 2012. For the first hypothesis, no further information was found; however, there is a high probability that these garments have been used in the past. Concerning the second hypothesis, this set shows a composition closer to the model (as confirmed by IR spectroscopy). However, possible additives may not have been detected due to their lower concentration. Finally, regarding the case studies production, the artificial leathers could have resulted from different production processes and/or different finishing treatments (shinny or suede look, flat or highly textured).

The micro visual assessment of their condition can be obtained from the analysis of Fig. 3.39, where both surface (Fig. 3.39a,b) and cross-sections (Fig. 3.39c) are analysed. As shown, the evolution from fair to unacceptable conditions is clearly related to the formation of white products at the surface (Fig. 3.39a–e). While whitish spots/stains are the first signs of acid formation (Fig. 3.39b,c), further degradation leads to the clear formation of white crystals of adipic acid (Fig. 3.39d,e). These products can be easily removed from the surface and do not show any type of adhesion to the top coating. Regarding the brown leather, although the macroscopic assessment lead to the attribution of 'good' within the condition grades scale, the observation under the microscope detected cracks on the surface of the top coating, which resulted in the assignment of a fair condition. Therefore, cracks and whitish products can be described as the main deterioration signs of ester-based TPU coatings. Although some of the TPU top coatings show a slight fluorescence under blue-violet light (see Appendix V), the emitted colour and/or intensity was independent from their condition. From the analysis of the cross sections, the complex structure of these leathers is confirmed (as discussed in the section 2.2.2, focused on TPU-based materials) as well as the formation of adipic acid as a deterioration product exclusively related to the top coating (ester-based polyurethane) and not to inner layers such as the fibrous support or the intermediate adhesive. Therefore, the formation of adipic acid can be related to the interaction of water or moisture with the urethane-based top coating, as previously mentioned for ester-based PUR foams.

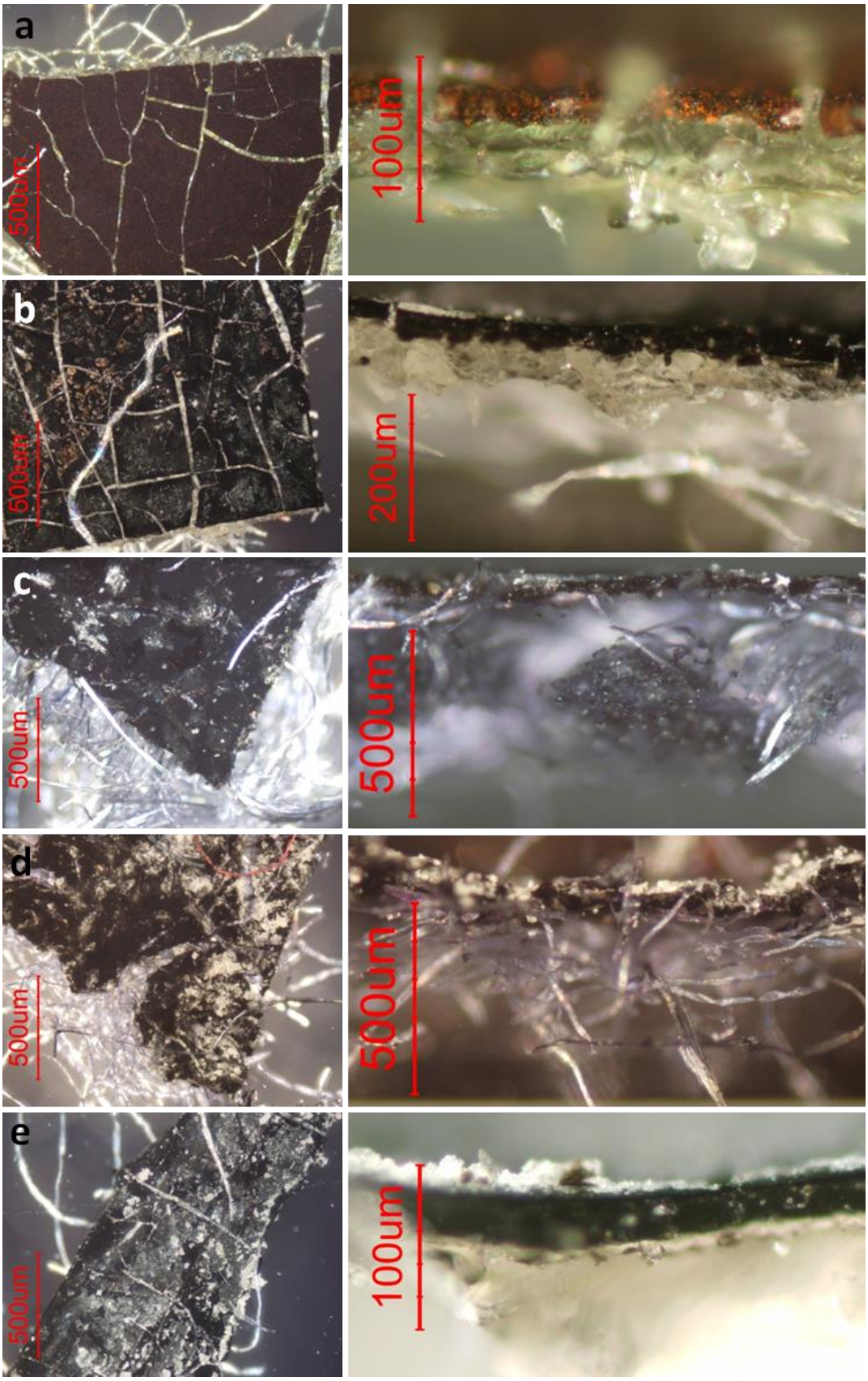


Figure 3.39 Microscopy images of TPU coatings collected from the historical fashion garments showing different condition grades under reflected cross-polarised light. Surface (left) and cross section (right). Fair condition grade: brown dress (a). Poor condition grade: less degraded areas from the blue long jacket (b) and the blue dress (c). Unacceptable condition grade: more degraded areas from the blue dress (d) and blue long jacket (e).

Regarding the infrared analysis, spectral changes were correlated to the deterioration of the TPU coating and possibly, to the disruption of H-bonds in TPU segregated structure. According to Fig. 3.40, from the unaged model (black) to the highly deteriorated coatings (grey spectra, Fig. 3.40d,e), several spectral changes are detected in the N–H, C=O and C–O–C stretching regions. While fair conditions are related to spectral changes in the N–H region (grey spectra, Fig. 3.40a); poor and unacceptable conditions show significant spectral variations in all regions of interest (grey spectra, Fig. 3.40b–e).

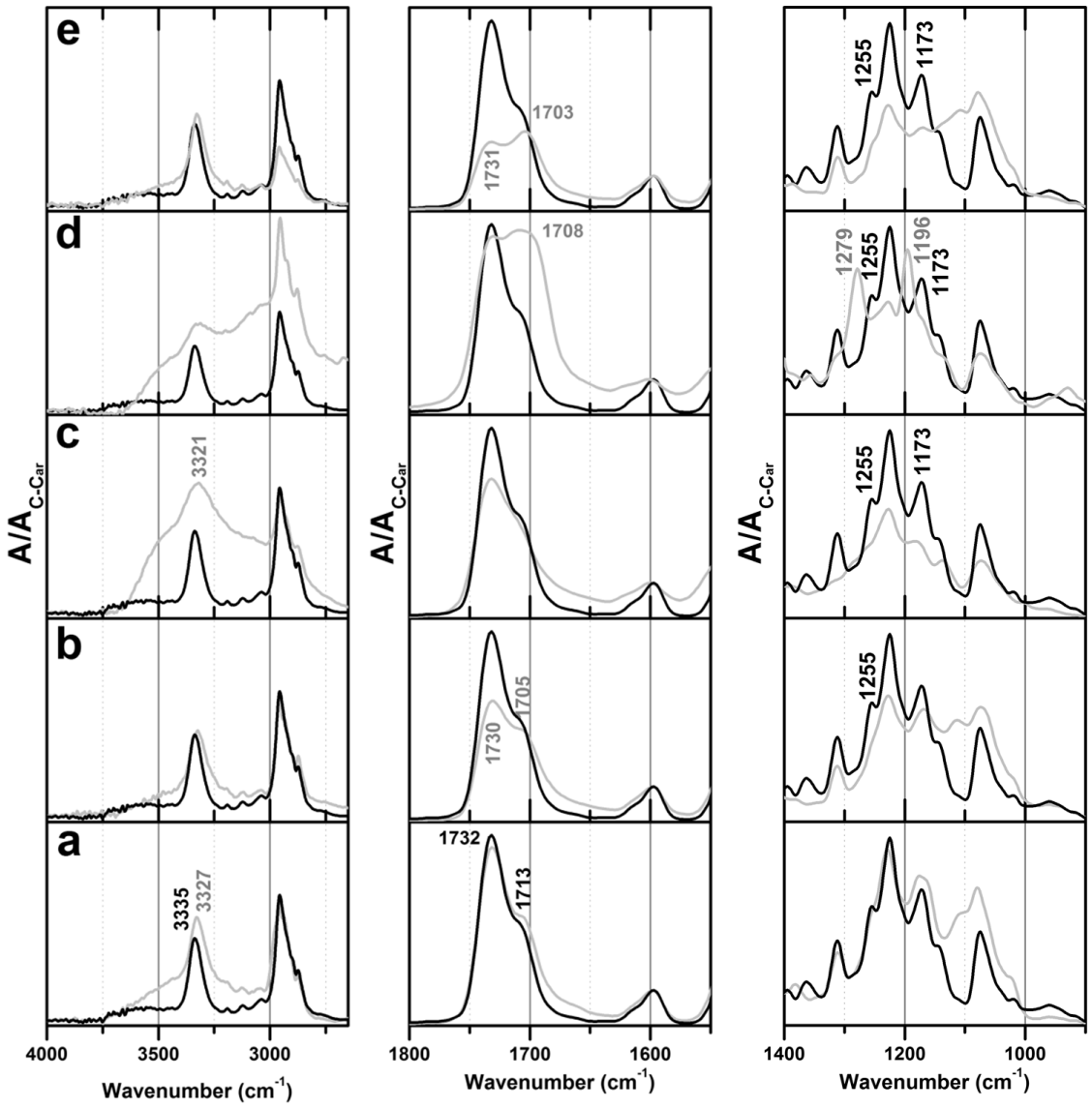


Figure 3.40 Infrared spectra of the unaged model TPU film (black) and the TPU coatings from the case studies from the MUDE collection (grey) showing different condition grades: N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). Fair condition grade: brown dress (a). Poor condition grade: less degraded areas from the blue long jacket (b) and the blue dress (c). Unacceptable condition grade: more degraded areas from the blue dress (d) and blue long jacket (e).

Poor conditions could be associated to the hydrolysis of the ester groups from the SS (cleavage of the SS and consequent decrease of the polymer molecular weight), leading to the formation of OH species and to the subsequent increase of the acidic content in the polymer backbone. As shown, bands assigned to ester groups (at 1732, 1255 and 1173 cm^{-1}) decrease in its relative intensity (Fig. 3.40b,c), causing the increase of the band between 3650–3400 cm^{-1}, assigned to N-H groups free of H-bonds and to the formation of O–H species (Fig. 3.40c). Unacceptable conditions (Fig. 3.40d,e), on the other hand, already show the clear precipitation of adipic acid as white crystals (Fig. 3.40d,e and Fig. 3.41). As shown in Fig. 3.40d,e, this could be translated in the infrared spectra by the appearance of bands related to high acid contents (in this case, adipic acid: broadening of the band at c. 1708 cm^{-1} and appearance of bands at 1279 and 1196 cm^{-1}) in the polymer matrix (Fig. 3.40d), or, by the high relative intensity decrease of the bands assigned to the SS domain, reflecting the destruction of the polymer 3D network: decrease of the C-H bands between 3000–2800 cm^{-1} and decrease of the C=O band at 1731 and the C-O-C bands at 1255 and 1173 cm^{-1}.

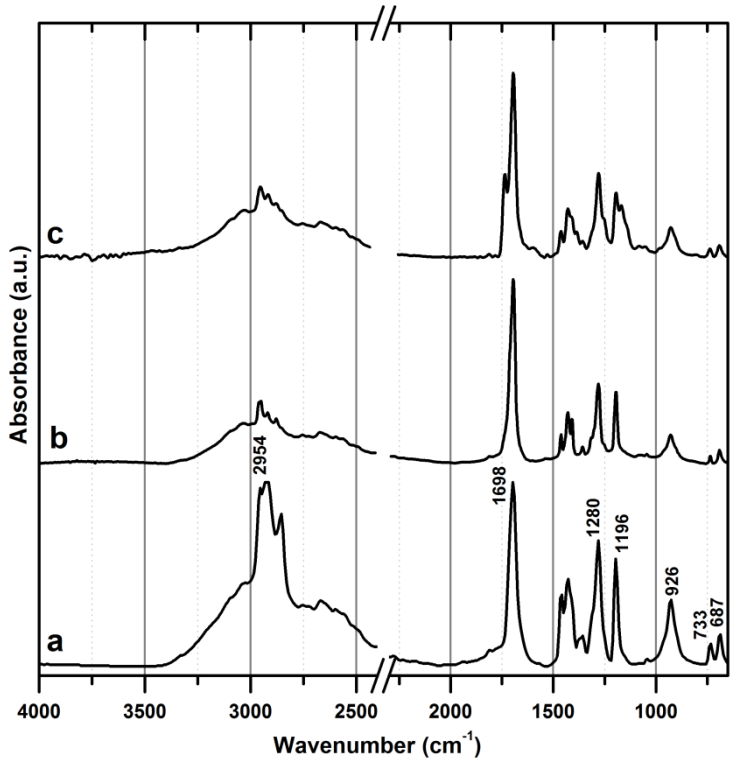


Figure 3.41 Infrared spectra of adipic acid 99+% reference (a) and the white crystals collected from the case studies (b,c): blue dress (b) and the blue long jacket (c).

Regarding the hydrogen-bonding interactions, several conclusions could possibly be drawn from the cautious analysis of these infrared spectra. As stated in the literature, the 'hydrogen-bonded morphology provides the distinctive elastomeric thermal and mechanical properties of the material'

(Schnoonover *et al*., 2001: 88). As a result, 'Understanding the property structure relationships and hard-soft domain interactions in these systems is important to gaining additional insight into the material's properties' (Schnoonover *et al*., 2001: 88), or in this case, to understand how natural ageing processes (as shown by these historical garments) affect the polymer micro morphology.

The typical following of H-bonds by monitoring C=O and N–H stretching regions is hampered in ester-based polyurethanes since this type shows a high potential to form carboxylic acid and alcohol groups during ageing (masking possible changes related to H-bonds). Moreover, the TPUs in study do not show urea linkages, i.e., there is no band at c. 1640 cm^{-1}. For that reason, other regions should be considered to assess the changes in H-bonds during the ageing of these TPUs. According to a study by Schnoonover *et al*., other bands can be considered to this end. For example, the band at 1228 cm^{-1} is assigned to both H-bonded C–N stretching and N–H bending, and the band at 1174 cm^{-1} to H-bonded C–O–C stretching (Schnoonover *et al*., 2001). Accordingly, by monitoring these two bands, the physical crosslink of ester-based TPU may be followed. Based on the IR assessment of the historical garments (from fair to unacceptable conditions), the significant decrease and shift of the band at 1225 to 1228 cm^{-1} is observed, along with the decrease and disappearance of the band at 1173 cm^{-1}, probably indicating the disruption (or weakness) of H-bonded groups in the polymer network and the subsequent disarrangement of its structure. Based on the Tian *et al.*'s study, ester-based TPU samples can suffer an increase in the degree of phase mixing when exposed to gamma irradiation in air and water (Tian *et al*., 2015). From the use of techniques such as small-angle neutron scattering (SANS), FTIR, gel permeation chromatography (GPC), and X-ray diffraction (XRD), Tian and co-authors detected both an increase of domain distance and decrease of domain size in TPU samples exposed to gamma irradiation (Tian *et al*., 2015). This finding confirms the instability of H-bonds in TPUs, when exposed to artificial ageing conditions. Regarding the case studies assessment, as the bands assigned to H-bonds (by Schnoonover) showed also significant spectral changes (when compared to model at t=0), these secondary bonds may be also susceptible to natural ageing conditions. Nevertheless, and once more, ageing experiments were carried out on model samples and similarly to previous sections, the model was submitted to natural (outdoor) and artificial (UV-Vis radiation, λ>300nm) ageing. The discussion in following section is limited to the natural (outdoor) ageing experiment since results closer to the historical garments were achieved.

3.5.3 Ageing experiments for the model sample

Based on optical microscopy, the model exposed to outdoor conditions has suffered significant visual changes after three and six months (Fig. 3.42). As shown, the previous flat, clean, smooth and shiny surface (Fig. 3.34) suffered discolouration, lost transparency and the surface gained a whitish layer

(Fig. 3.42, on the left) easily removed by scratching the surface. The whitish layer became more visible after six months and white compounds started to appear at the surface of the film (Fig. 3.42b, on the left). Regarding the fluorescence images, once more, a higher intensity is observed on the aged films (as observed in previous sections). In general, with the exception of the formation of cracks (absent in this ageing), similar visual decay with the TPU top coatings from the historical garments was observed, i.e., the formation of white powders at the surface. Therefore, the cracks may be associated to continuous use and wearing of the garments. Furthermore, the TPU samples were deposited into glass slides, which offer a greater resistance than textile supports, as found on the historical case studies.

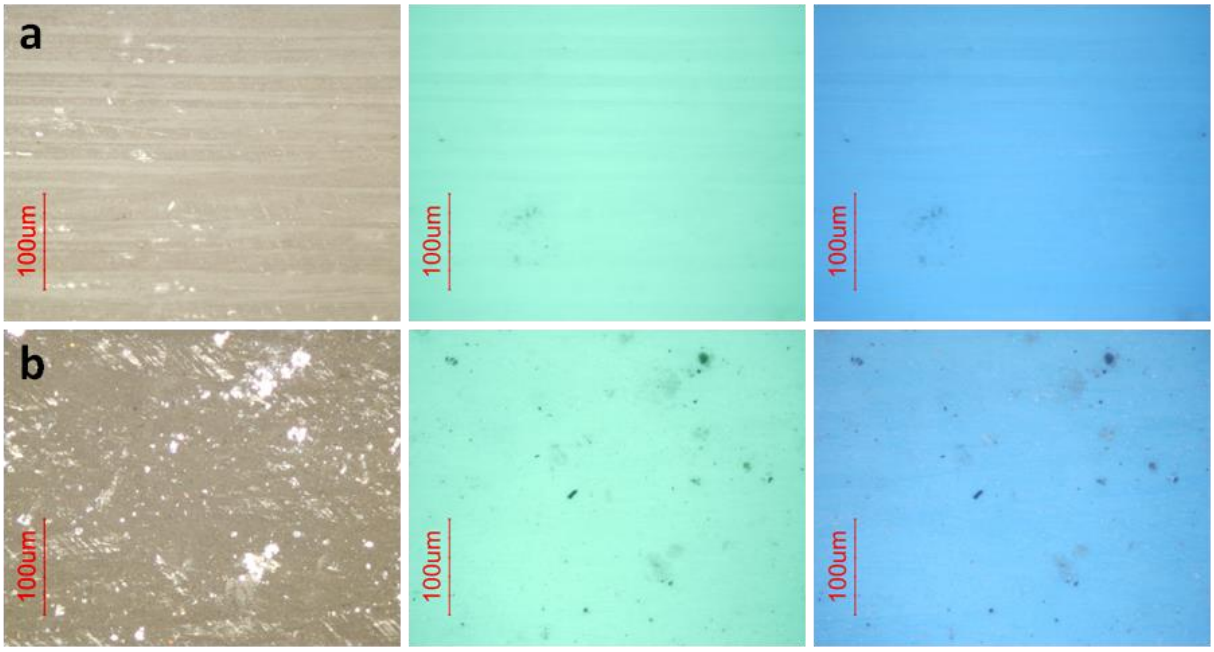


Figure 3.42 Microscopy images of the model TPU film after three (a) and six (c) months of natural (outdoor) ageing under reflected cross-polarised (left), blue-violet (centre) and ultraviolet light (right).

From infrared analysis, similar molecular decay was observed, especially with the case studies showing poor conditions (Fig. 3.40b,c and Fig. 3.43). The ageing has resulted in spectral changes in all regions of interest. A decrease of the bands at 1732, 1255, 1225 and 1173 cm^{-1} is observed, along with the decrease of the C–H bands between 3000–2800 cm^{-1}. This proves that the most affected bands are assigned to the ester-based SS, and that the ageing of TPUs could once more be related to the disarrangement of their ordered structure (HS domain), possibly caused by the increase of phase mixing (as suggested for the case studies).

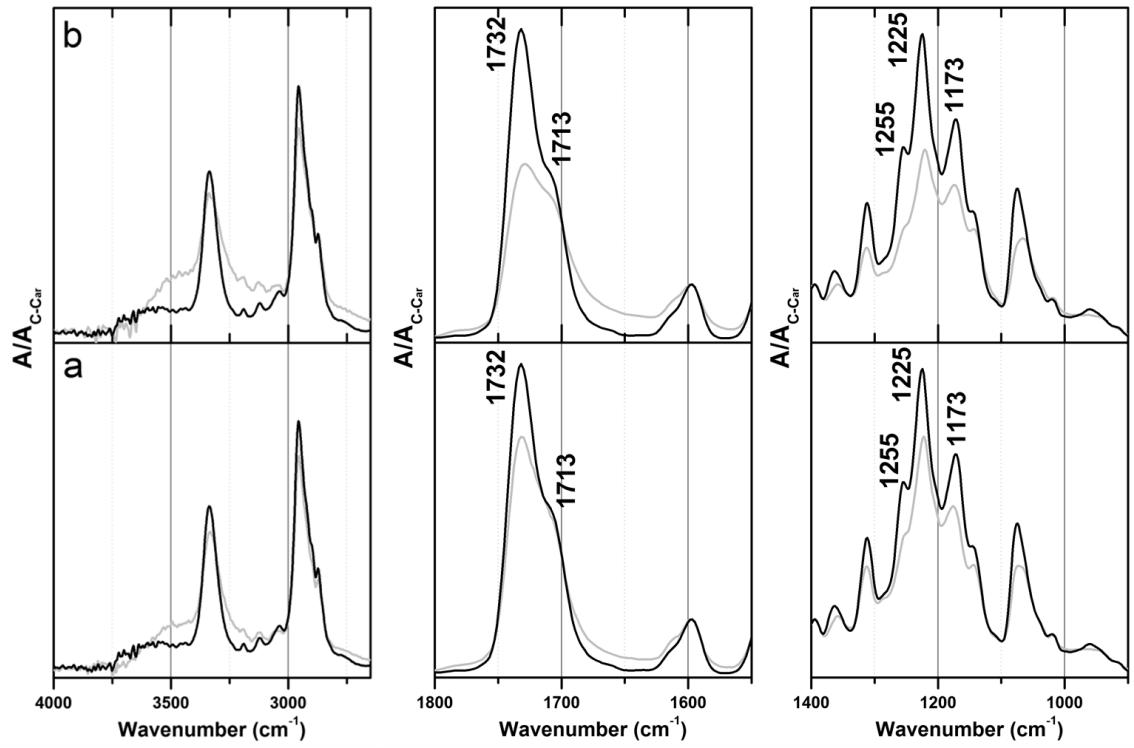


Figure 3.43 Infrared spectra of the model TPU film before (black) and after (grey) natural ageing (outdoor): N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). After three (a) and six (b) months of ageing.

As polyurethane elastic fibres have also been left aside (in general) from conservation studies, the following section includes a brief discussion about two case studies from the MUDE collection. However, the presented study is only a preliminary research: only two textile objects are included, no unaged models (references) were produced for comparison and no ageing experiments were conducted. Still, promising results were obtained, drawing attention to the presence of this material in museum collections and to the conservation issues raised by them.

3.6. Ether-based TPU fibres

Polyurethane fibres are generally known under the trade name *Spandex*[84] (USA) or *Elastane* (Europe) and may be found in museum collections in elastic fabrics, clothes and/or accessories (van Oosten, 2011). As stated by W. D. Schindler, 'In the meantime about half of all clothing fabrics contain elastane fibers [or spandex] and around 85% of elastane fibers are used for clothing' (Schindler, 2009: 312). In

[84] *Spandex* is the trade name of an 'elastomer of at least 85% of a segmented polyurethane' (Lowry *et al*., 1985 as cited in Tungol *et al.*, 1990: 547).

recent years, the fast degradation rate of these fibres has been recognised by conservators, mostly from fashion collections (Marjo *et al*., 2016). Consequently, being polyurethane commonly known for its short lifespan, the presence of these materials in museum collections may raise issues that should be addressed in their own specificity. An example of their fast degradation is shown in Fig. 3.44, where the elastic fabric of a pair of cycling shorts (c. 2005) is completely misshapen since 2012 due to the break-down of the elastomeric polyurethane fibres (white).

Figure 3.44 Microscopy image under reflected cross-polarised light showing a highly degraded elastic fabric from a pair of cycling shorts (c. 2005). The fabric is made of elastomeric polyurethane fibres (broken white filaments) and polyamide fibres (dark reddish filaments). Condition of the elastic fabric in 2012.

3.6.1 Preliminary study of historical ether-based TPU fibres

To contribute to knowledge regarding the degradation of polyurethane fibres, two textile objects from the MUDE collection were selected as case studies (Fig. 3.45). These were two swimsuits (c. 1976) designed by Roy Halston (USA, 1932–1990) showing an elastic fabric of dark blue colour. Given the

high elasticity of the fabric, the presence of elastomeric fibres[85] (e.g. polyurethane or rubber yarns) in a blended fabric was posed as a hypothesis (as identified in some patents discussed in Chapter 2).

Figure 3.45 Polyurethane fibres case studies from the MUDE collection. Roy Halston, right cut out and one shoulder swimsuit (c. 1976) (second from the left) and Roy Halston, one shoulder swimsuit (c. 1976) (third from the left). Photo: ©MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

The two selected objects show different conditions. In one case the elastic fabric maintains its resilience, recovering the original position when stretched (enabling the display on mannequins), whereas the other yellows the materials nearby, releases a strong odour (which can be described as stinging and acrid), and the fabric has sagged due to weak recovery when stretched. Aiming at getting a visual and molecular insight into their condition, the swimsuits materials were characterised by IR spectroscopy and optical microscopy.

Based on IR spectroscopy, a blended fabric composed of polyamide (higher percentage) and elastomeric polyurethane (minor percentage) fibres was identified (Fig. 3.46).

[85] According to James Gordon Cook, 'Elastomeric fibres are those which display elasticity characteristics associated with natural rubber; they will stretch to several times their original length, and on release will snap back quickly to recover their original length almost completely (Cook, 1984: 611). For example, in the case of polyurethane filaments, 'The elongation to break of spandex fibers is typically over 200%, and more often in the range of 400–800%' (Yin *et al.*, 2014: 16).

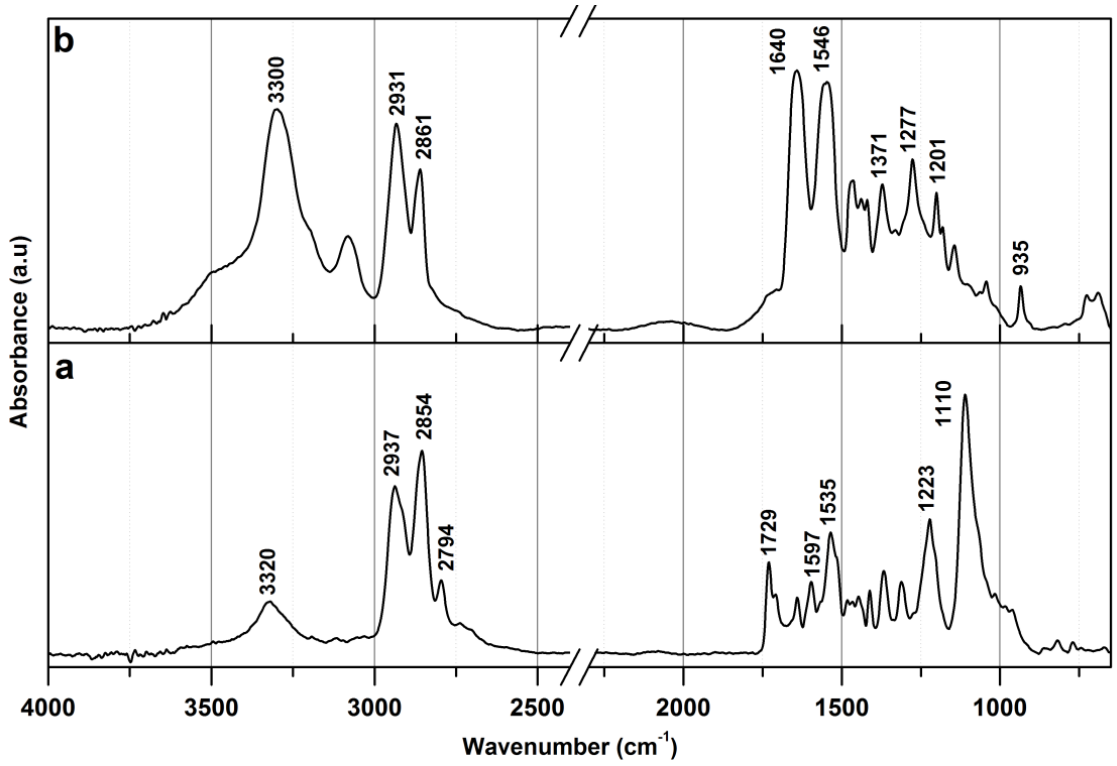


Figure 3.46 Infrared spectra of the blended fabric from the two swimsuits: polyurethane (a) and polyamide (b) fibres.

The polyamide spectrum shows the characteristic bands of nylon: the bands at c. 3300 cm^{-1}, c. 1640 cm^{-1} and c. 1545 cm^{-1} are assigned to N–H stretching, C=O stretching, and both C–N stretching and N-H bending, respectively, (Fig. 3.46b) (Tungol *et al*., 1990; Montaser *et al*., 1991; Vasanthan & Salem, 2001); whereas the polyurethane spectrum shows a strong band at 1110 cm^{-1}, assigned to the C–O–C group from the ether-based SS, and the bands at c. 1600 cm^{-1} (C=C stretching) and c. 1535 cm^{-1} (C–N and N–H), assigned to the aromatic rings and urethane groups, both from the HS of the TPU (Fig. 3.46a). In the Renier *et al*.'s study, an IR spectrum with high similarities with this TPU was found (Renier *et al.,* 1994). As a result, it might be said that the TPU fibres from the case studies are likely produced from poly(tetramethylene ether) glycol (PTMEG) (as the SS) and poly(urethane)-poly(urea) copolymers chain extended by diamines (as the HS) (Renier *et al.,* 1994). However, the path taken to get to this identification (sampling and analysis) was not a linear process, and the followed methodology is described in the following paragraphs.

According to Espinoza *et al*., 'the characterization of fiber blends presents a unique challenge' (Espinoza *et al*., 2006: 386). This is especially true when (i) the ratio of the different fibres is highly disproportional, making difficult the sampling and characterisation of the fibre in the lowest percentage; (ii) when sampling is not allowed; or, (iii) in the case of sampling, when fibres show similar dimensions, shapes and colour, making their visual distinction difficult for collection. Since elastomeric

fibres are commonly invisible (i.e., hidden with the weave structure of the fibre in the highest percentage), sampling requires stretching. If the garment shows clear signs of ageing, irreversible damages can be caused by the stretching step, making this approach particularly harmful and avoidable in conservation procedures (Garside, 2009).

To overcome these obstacles and to identify the composition of the fibres, different approaches were sought. At first, FTIR-ATR with no sampling was attempted. However, the low percentage of the elastomeric fibre and its presence in the in-depth layers resulted in the failure to identify the fibre. This was already acknowledged by other researchers when facing similar problems (Espinoza *et al*., 2006). Then, the collection of single fibres (isolation of individual fibres) within the fabric structure was carried out without stretching the fabric, since this would cause damages. Nevertheless, only polyamide fibres (fibres with highest ratio in the fabric) were sampled and the presence of elastomeric fibres remained unidentified. Finally, to detect the presence of the fibres in the lowest ratio, samples with c. 2mm length were collected from the reverse side of the swimsuits, and on the extra fabric that crosses the sewing line. This approach has been proposed by the textile conservator, P. Garside, in cases where sampling is required (Garside, 2009). Although this method has the disadvantage of requiring the sampling of a larger sample, it was the only method allowing the molecular identification of the two different fibres, a deeper insight into their visual aspects, and the clear detection of visual signs possibly related to ageing[86].

The observation of the fabric sample under the microscope allows a distinction between the two fibres (polyamide and the elastomeric fibre, polyurethane) (Fig. 3.47). From different illumination modes, their distinct texture (Fig. 3.47a, on the left) and structure (Fig. 3.47a, on the right) is observed, confirming optical microscopy as a powerful tool for the analysis of synthetic fibres, as supported by the literature (Espinoza *et al*., 2006; Lee *et al*., 1997; Garside, 2009). By using polarised light microscopy and fluorescence microscopy, distinctive and complementary information has been obtained. Under reflected cross-polarised light, the polyurethane fibres show a matt coloured surface composed of micro dots[87] and a white core; and the polyamide fibres, a bright, coloured and smooth surface. From fluorescence under blue-violet light, structural features (such as morphology) of the fibres have been highlighted[88]. The polyurethane fibre comprises four independent filaments composing a clover shape structure (partly-fused filaments), while the polyamide fibre shows two individual thin filaments, partly-fused together.

[86] The assessment of the swimsuit condition was carried out from the observation of this unique sample in order to avoid the collection of additional samples in the swimsuit.

[87] According to a personal communication by Anita Quye, these micro dots can be due to the presence of inorganic fillers, opacifiers, anti-UV agents or pigments.

[88] As no further information was observed from the observation of these fibres under ultraviolet light, these images were not collected.

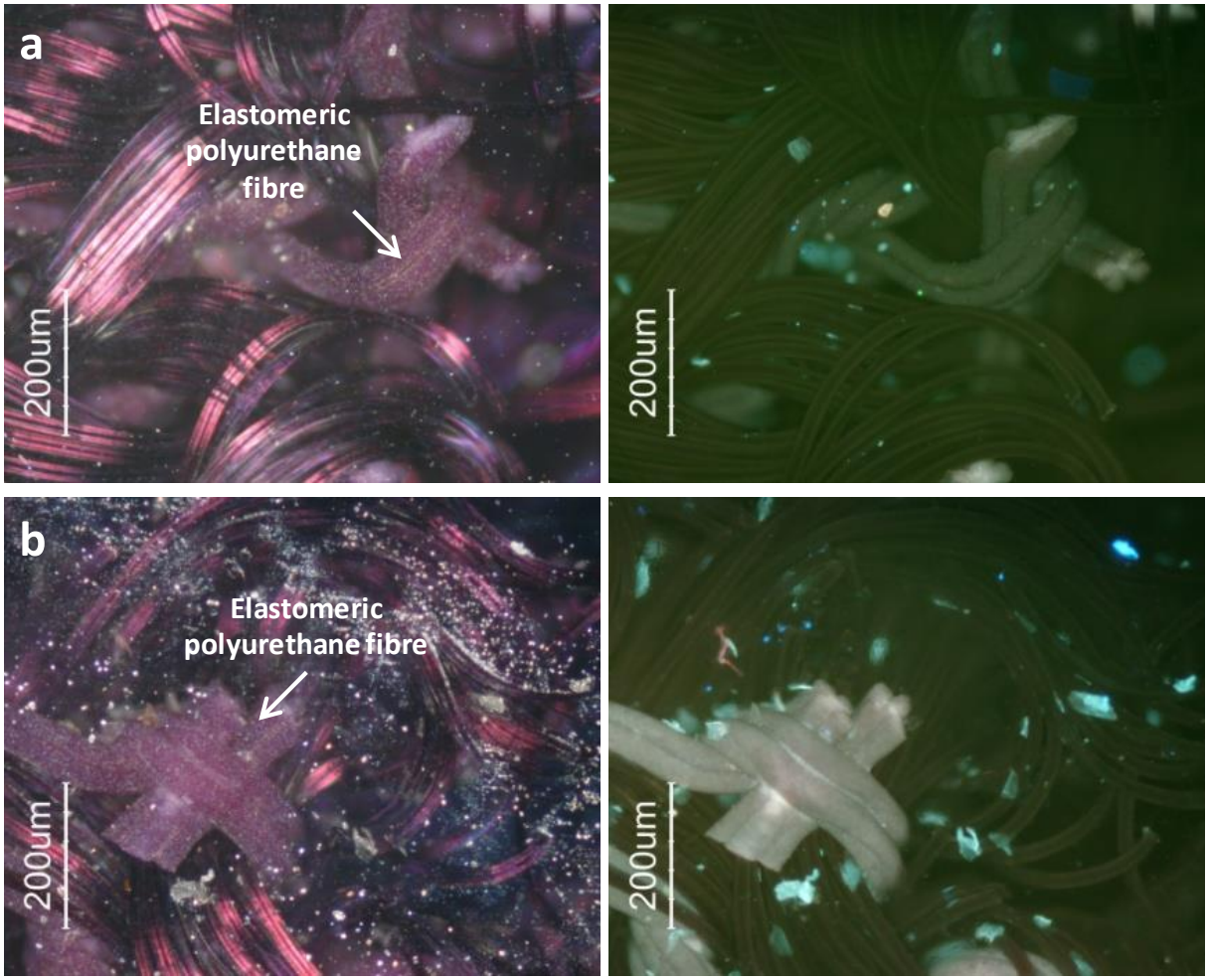


Figure 3.47 Microscopy images of the elastic fabric collected from the historical fashion garments showing blends of fibres (polyurethane and polyamide) and different condition grades under reflected cross-polarised light (left) and blue-violet light (right). Fair condition grade: one shoulder swimsuit (a). Poor condition grade: right cut out and one shoulder swimsuit (b).

According to Lee *et al*., polyurethane fibres based on the previously proposed raw materials[89] follow dry spinning processes[90] (Lee *et al*., 1997), which were extensively used commercial processes for TPU fibres when the swimsuits were made (Lee *et al*., 1997; Otaigbe & Madbouly, 2009). According to U.S. Patent 3,094,374 assigned to E. I. DuPont de Nemours and Company, 'It is well known that dry-spun spandex filaments are tacky immediately after extrusion', moreover, 'It is also known that bringing a group of such tacky filaments together will produce a coalesced multifilament bundle, which is then usually coated with talc before winding to prevent sticking on the package' (Smith, 1963: n.p.). This talc-finished product is described in this patent as having an abrasive effect on the fibre (Smith, 1963).

[89] PTMEG and poly(urethane)-poly(urea) chain extended by diamines – information obtained from the comparison of the IR spectra of the TPU fibres (from the selected textile objects) with the IR spectrum shown in the Renier *et al*.'s study (Renier *et al*., 1994).

[90] The dry spinning process uses a high volatile solvent and the fibre is formed during spinning by solvent evaporation.

Aside from talc, Otaigbe and Madbouly mention that finishing agents such as magnesium stereate and poly(dimethyl siloxane) can also be used (Otaigbe and Madbouly, 2009). Although it would be interesting to know if there is any relationship between the use of these finishing agents and the ageing of TPU fibres, to our knowledge, nothing was found in the literature.

By taking these statements into consideration, the research discussed in Chapter 2 (industrial patents), and one J. Gordon Cook textile publication (Cook, 1984), morphological features of fibres such as colour, thickness and shape might be used as markers to distinct TPU fibres from other elastomeric fibres (such as rubber) – the two most common elastomeric fibres used in clothes up to the 1970s. As discussed in Chapter 2, TPU fibres had a tremendous success as they could replace rubber threads with the offer of better properties. For instance, rubber threads are thicker (150 den) and difficult to dye (remaining white), whereas TPUs can be spun into extremely thin filaments (40 den or finer) and easily dyed. Consequently, rubber threads can never be found in textiles as multifilament yarns, but as covered rubber threads (rubber yarns wrapped by fibres such as cotton and nylon) and with square/rectangular (if cut from vulcanised sheet) or round (if extruded from latex[91]) cross-sections (Cook, 1984; van Voorhis, 1942). Conversely, TPU fibres are commonly found as bare (uncovered) filaments (single or multi); with each single filament showing round cross-sections, and in a wide range of colours and shades (Cook, 1984; Otaigbe & Madbouly, 2009)[92]. An additional hypothesis of an elastomeric fibre in this period (although rare) was the acrylic-based *Anidex*[93]. However, this fibre production was shortly discontinued due to the high success of spandex (Tortora & Johnson, 2013: 20). Accordingly, the classification of the present fibres as polyurethane and as a product of dry spinning processes gains validity since coloured, long, thin fibres (with c. 30 µm diameter each) are observed, a bundle of filaments is shown (multifilament yarns), and a superficial finishing is detected (micro dots, probably caused by the talc abrasion effect) (Fig. 3.47). All these aspects, observed under the microscope, highlight optical microscopy as a powerful tool to identify elastomeric TPU fibres. However, IR spectroscopy should always be carried out to accurately define the fibre chemical composition.

Regarding the swimsuits condition assessment, optical microscopy enabled the detection of visual aspects possibly related to ageing, especially from the fluorescence images under blue-violet light. As observed, micro particulate (Fig. 3.47b, on the left), and a higher fluorescence intensity (Fig. 3.47b, on

[91] Method introduced in the 1930s (Cook, 1984).

[92] TPU fibres can also be found as covered yarns, core-spun yarns and core-twisted yarns for foundation garment trade (Cook, 1984).

[93] 'A manufactured fiber in which the fiberforming substance is any long chain synthetic polymer composed of at least 50% by weight of one or more esters of a monohydric alcohol and acrylic acid (CH_2=CH–COOH) (FTC definition)' (Gooch, 2011: 40). Acrylic elastomeric fibre produced in 1969 by Rohm and Haas and commercialised under the tradename ANIM/8®; however, its production was discontinued shortly after due to the excellent properties of polyurethane elastomeric fibres (Tortora & Johnson, 2013: 20).

the right) is detected on the most degraded fabric. The use of fluorescence to detect effects of ageing on fibres has already been reported (Herman, 1998 as cited in Garside, 2009: 340). Nevertheless, to our knowledge, the study of ageing effects of polyurethane fibres by optical microscopy has not been focused in the literature due, probably, to the scarcity of conservation studies regarding these materials.

In this case, the more degraded polyurethane fibres can be described as stickier (probably causing the adhesion of dirt and particulate), less flexible (observations taken during handling) and with a more intense fluorescence than the less degraded. According to the professor of textile chemistry, W. D. Schindler, spandex fibres (in general) 'are particularly susceptible to thermomechanical damage (by heat and tension) and are also attacked and degraded by hydrolysis (acids and alkalis) and photolysis (especially by UV light) (Schindler, 2009: 312). Schindler states that 'When the conditions are not too aggressive they are stable to oxidizing and reducing agents', but in the presence of chlorine, heavy damages are caused (Schindler, 2009: 312). Since this swimsuit was probably used in the past (sand grains were found within the fibres), its exposure to chlorine (NaCl from sea water or chlorinated water in swimming pools) and UV radiation should be considered as a probable cause of degradation, mostly because ether-based SS are known for their higher susceptibility to photo-oxidation and chlorine, when compared to ester-based SS (Schindler, 2009). Aside from this, 'Photolysis causes discoloration as well as loss of strength and elasticity or even fiber breakage' (Schindler, 2009: 314), which 'can be accelerated by oils and skin creams' (Schindler, 2009: 315). From these statements, the higher fluorescence intensity of the most degraded polyurethane fibres might be explained.

To complement the information obtained, individual TPU fibres were sampled from each swimsuit and analysed by optical microscopy under transmitted polarised light. This method has been commonly applied to study optical properties of fibres such as pleochroism (or dichroism)[94], birefringence[95], sign of elongation[96] and interference colours[97], among others (Palenik, 2003; Petraco & Kubic, 2003; De Wael *et al*., 2012; Carlton, 2011). For instance, 'man-made fibres can be recognized by their interference colours when viewed between crossed polars at 45° between the extinction positions through a 1st-order Red Plate added to the lens system' (Farnfield & Perry, 1975: 138). An example showing the useful application of this method is described by Farnfield and Perry when analysing

[94] Colour change on stage rotation under plane-polarised light (Palenik, 2003; Carlton, 2011). According to De Wael *et al*., 'In textile fibres, only two main orthogonal directions are considered, which correspond to the fibre long axis and to its perpendicular direction', and 'Fibres possessing linear dichroism show differences in hue and/or intensity when observed with plane-polarised light of different orientation' (De Wael *et al*., 2012: 249).

[95] Numerical difference between high and low (two principle) refractive indices (Carlton, 2011). It 'Provides a measure of the molecular orientation of the polymer chain of the fiber' (Broadbent, 1999).

[96] Relationship between a fibre's length (or long axis) as it relates to its refractive indices (Petraco & Kubic, 2003). As stated by Carlton, 'For elongated uniaxial crystals (and fibers that act like uniaxial crystals), if the high index is associated with the length then the sign is positive, negative otherwise' (Carlton, 2011: 21).

[97] Colour of a specimen between cross-polars. This property depends on the specimen birefringence and thickness, as well as on the orientation of the incident light (Carlton, 2011).

acrylic and acetate fibres (Farnfield & Perry, 1975: 138–139). For the present study, this method has been used. A test plate with the rotatable compensator Lambda (+/-8° 6x20)[98] was applied in combination with transmitted CPL. However, in the present research, it has been concluded that the colour of the polyurethane fibres remained dark (extinct) as stage rotates (Fig. 3.48a, compare left and right images).

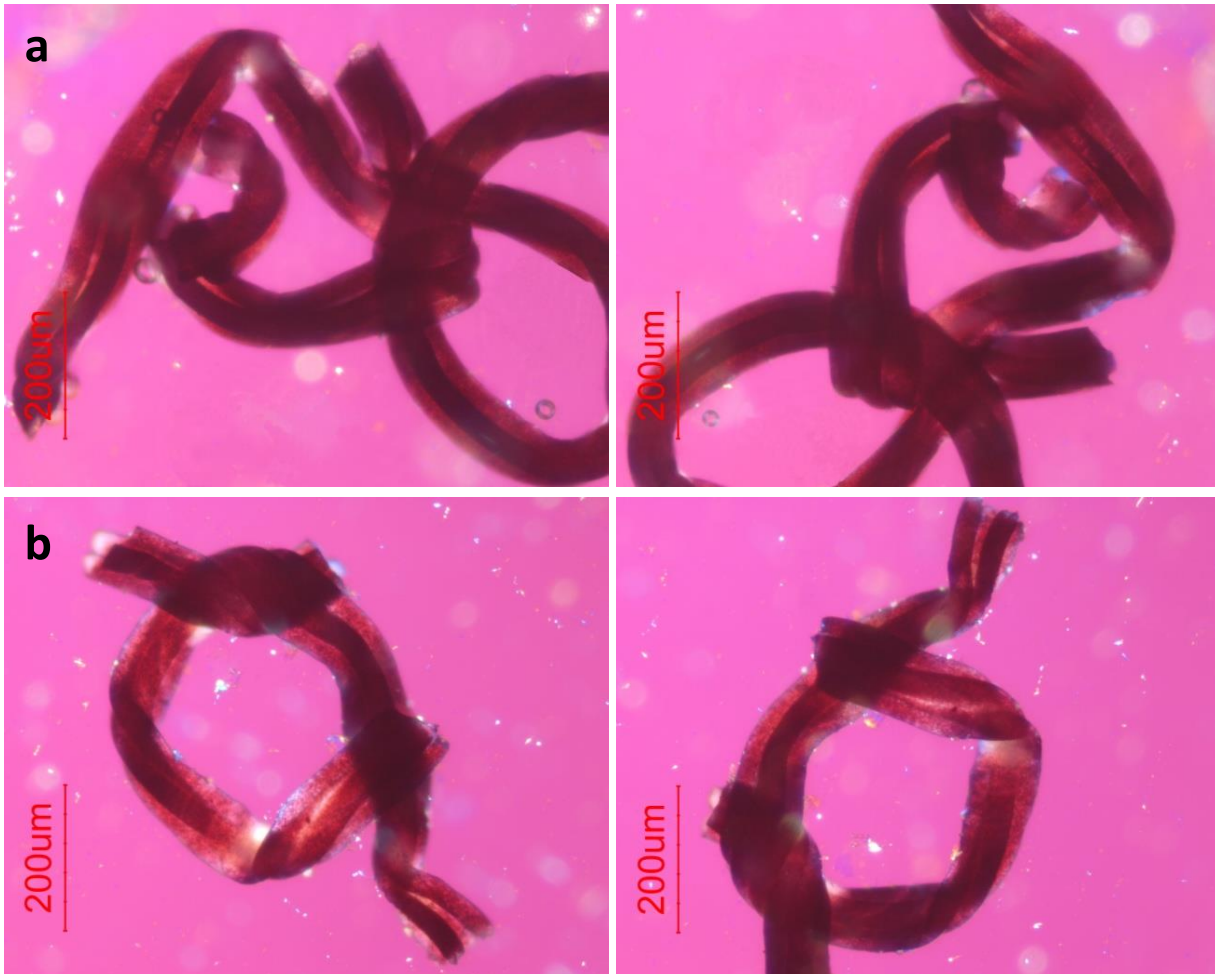


Figure 3.48 Microscopy images of elastomeric polyurethane fibres collected from the historical fashion garments showing different condition grades, under transmitted cross-polarised transmitted light with Lambda compensator. Fair condition grade: one shoulder swimsuit (a). Poor condition grade: right cut out and one shoulder swimsuit (b).

This can be related to their almost optically isotropic property and birefringence close to zero (Petraco & Kubic, 2003: 87), along with their opaque colour, which results in fibres which are unaffected by

[98] Also known as first order (or full wave) retardation plate, red plate, lambda (λ) plate, etc. According to Davidson, 'The first order retardation plate is a standard accessory that is frequently utilized to determine the optical sign (positive or negative) of a birefringent specimen in polarized light microscopy', and 'for enhancing contrast in weakly birefringent specimens' (Davidson, 2012).

rotation under PPL and CPL (De Wael *et al*., 2012). On the other hand, different opacity levels have been observed between the fibres showing fair (Fig. 3.48a) and poor (Fig. 3.48b) conditions. The fibres that looked in the worst condition are more transparent than the fibres in better condition. Unfortunately, due to the lack of studies on polyurethane fibres, this relationship between condition and fibre opacity is not possible to confirm.

Since the swimsuits were produced by the same designer, at the same time and probably, with the same fabric, the visual differences detected between the fibres in fair and poor conditions may be a product of different ageing processes. Accordingly, distinctive IR molecular fingerprints are also expected, which would allow the identification of spectral changes related to ageing. However, when the two spectra are compared, no significant differences are observed (Fig. 3.49). Only small variations in the C–H (3000–2750 cm^{-1}) stretching region are detected, as well as minor changes in the C=O (1750–1600 cm^{-1}) and C–O–C (1110 cm^{-1}) stretching regions (Fig. 3.49).

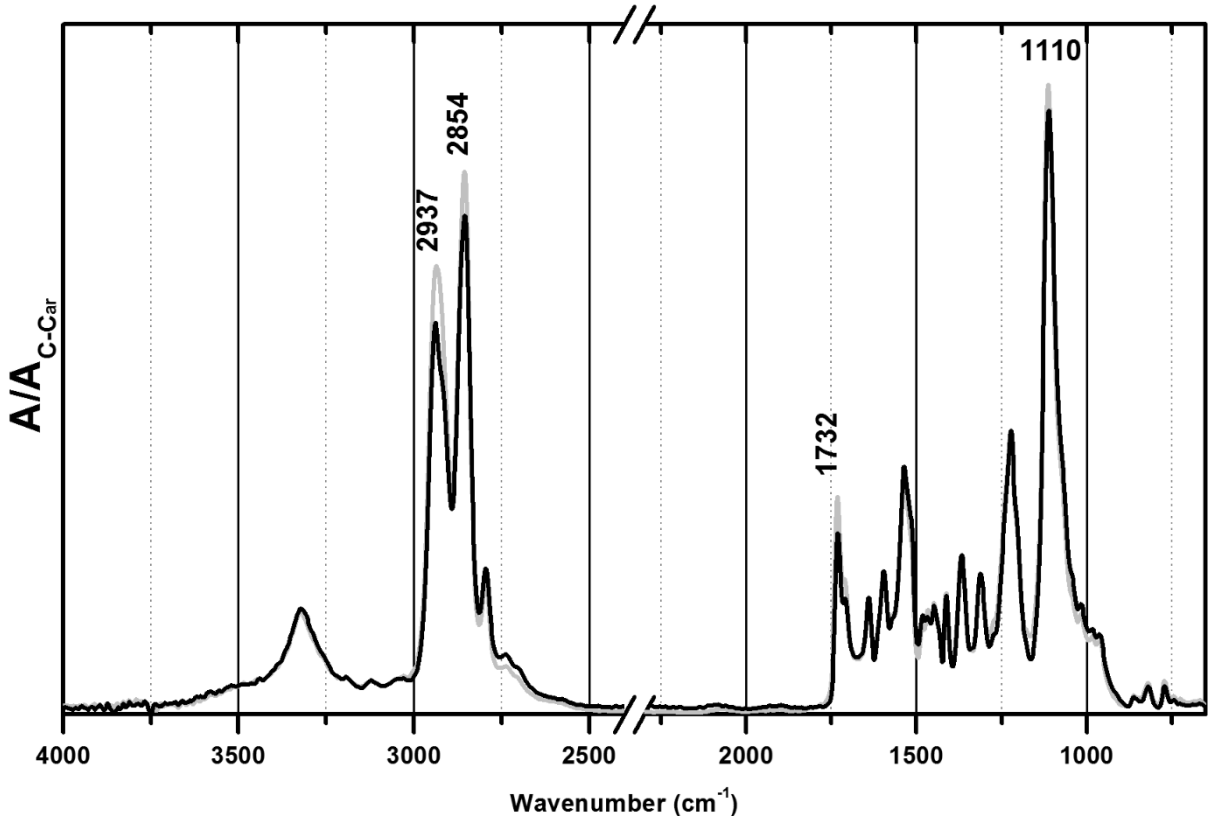


Figure 3.49 Infrared spectra of the elastomeric polyurethane fibres collected from the historical fashion garments showing different condition grades. Fair condition: one shoulder swimsuit (black). Poor condition: right cut out and one shoulder swimsuit (grey).

To attempt the confirmation of these variations as ageing consequences, an infrared spectrum of a polyurethane elastomer[99] from a library database was selected for comparison (serving as an unaged reference). This reference shows high similarities with the case study spectra (compare Fig. 3.49 with Fig. 3.50) and with the polyurethane elastomer studied by Renier *et al.* (Renier *et al.,* 1994: 233).

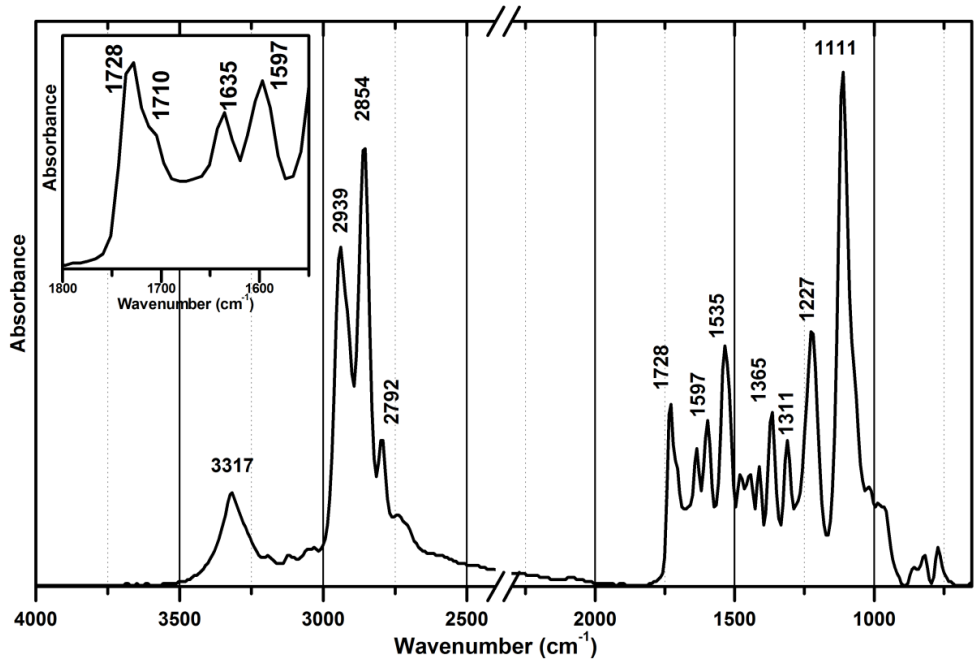


Figure 3.50 Infrared spectra of the polyurethane reference.

By comparing both case studies and reference spectra, the new detected spectral lines may enable the translation of visual ageing into specific molecular fingerprints (Fig. 3.51). Based on IR spectroscopy, noteworthy differences in bands relative intensity assigned to C–H and C–O–C stretching regions (SS) are detected between the reference (Fig. 3.51, black spectra) and the case study TPU fibres (Fig. 3.51a,b grey spectra). As shown, the grey spectra have higher intensities in both these regions. However, according to Gaina *et al*., these spectral variations may not be related to ageing, but to different Mw of the raw materials, which in this case, may reflect SS (in the polyurethane fibres from case studies) with higher Mw (Gaina *et al*., 2013). Gaina *et al*. supports that different Mw are reflected by changes in the bands assigned to C–O–C (at 1105 cm^{-1}) and to C–H (3000–2750 cm^{-1}), and higher Mw result in higher absorptions (Gaina *et al*., 2013). As polyurethane elastomeric fibres usually

[99] The infrared spectrum of polyether urethane was acquired from the Hummel Polymer Additives Library database, Index 212, manufacturer Ethicon Biomer. The spectra of this library were compiled by Dr. Dieter O. Hummel at the Institut fur Physikalishche Chemie der Universitat Koln. The bands at 2939, 2854 and 2792 cm^{-1} (C–H stretching), 1365 cm^{-1} (C–H wagging) and 1111 cm^{-1} (C–O–C stretching) are assigned to the ether-based soft segment; and the remaining bands to the hard segment (see structures of SS and HS in Chapter 1). The most important are recorded at 3317 cm^{-1} (N–H stretching), 1728 and 1635 cm^{-1} (C=O stretching), 1597 cm^{-1} (C=C stretching), 1535 cm^{-1} and 1227 cm^{-1} (C–N stretching and N–H bending).

comprise SS with Mw in the range 1000–3000 (Schindler, 2009), the higher absorbance intensities of the case studies spectra might be caused by higher Mw of the polyol. Consequently, only the C=O stretching region can be assessed for the identification of spectral variations related to ageing (Fig. 3.50a,b, on the centre).

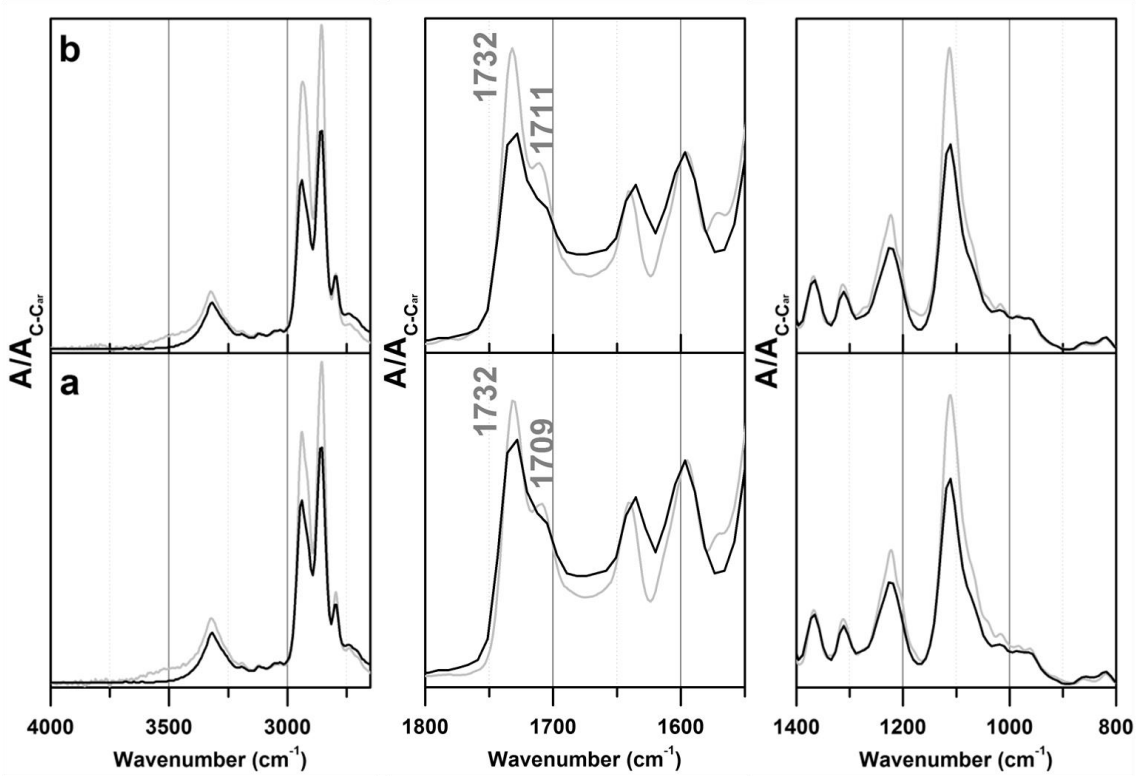


Figure 3.51 Infrared spectra of the reference (black) and the elastomeric polyurethane fibres collected from the case studies from the MUDE collection (grey) showing different condition grades: N–H and C–H stretching regions (left), C=O stretching region (centre) and C–O–C stretching region (right). Fair condition grade: one shoulder swimsuit (a). Poor condition grade: right cut out and one shoulder swimsuit (b).

From the less to the most degraded fibres, an increase at 1732 and 1711 cm^{-1} is recorded, possibly indicating the formation of new hydrogen-bonding interactions on the urethane linkages from the HS, or the formation of new C=O species due to the oxidation of the ether-based polyol. Curiously, no spectral changes in the urea band (at c. 1640 cm^{-1}) were detected. Since this band was confirmed as an extra marker of PUR foams condition upon ageing, shifts and/or band increases were expected to be observed in these cases. Instead, nothing was registered. On the other hand, the absence of changes in the C=O urea band has been observed by Khatua and Hsieh when studying the effect of chlorine degradation on polyurethane fibres (Khatua & Hsieh, 1997). As the swimsuits were probably used in the beach (as explained before), and the effect of chlorine degradation does not affect the urea

band (at c. 1640 cm^{-1}) (Khatua & Hsieh, 1997), this may indicate the exposure to chlorine as the main degradation source of the degraded swimsuit.

Still, as these materials have been poorly studied by optical microscopy and infrared spectroscopy and only out-of-date studies were found (focusing mostly physical properties) (Yokura & Niwa, 1988; Epps, 1987), the assignment of the detected spectral changes should be regarded as preliminary conclusions. Overall, this preliminary insight contributes to a higher knowledge about both visual and molecular changes occurring during the ageing of polyurethane elastomeric fibres as found in museum collections. It also highlights the use of optical microscopy has a powerful tool for the characterisation of conditions.

3.7. Conclusions

In this chapter, a new insight into the deterioration of PUR is proposed. Based on IR and optical microscopy (OM) assessment of PUR-based historical objects (from the MUDE collection) and aged references, a visual course and molecular pathway for PUR deterioration is suggested. As the selected historical objects showed condition grades from fair to unacceptable, several stages of PUR degradation have been assessed, and this in-depth analysis has benefited from a comparison with unaged models (t=0), which were produced for this research. Systematic differences have been identified (between models and case studies), making it possible to design a deterioration scale for PUR, and to suggest an ageing pathway for each PUR type and form that has been studied in this research. The production and characterisation of models was crucial to translate early signs of deterioration into new spectral lines. This was imperative in cases where ageing was clear under the microscope but not by IR spectroscopy, which only revealed small variations in bands relative intensity by comparison with the unaged model. Furthermore, the production of models has allowed the identification of infrared markers to distinct PUR types as well as production processes. For example, for the first-time, infrared markers have been proposed for the identification of ether-based PUR foams following cold-mould productions.

To verify if the differences detected between the unaged models and the case studies were reproducible (and representatives of ageing tendencies), models have been submitted to natural and artificial ageing experiments. As the ageing results were comparable to the PUR-based case studies, a correlation has been established, and specific visual changes (at the micro level) have been translated into molecular fingerprints in the infrared. This allows expanding the current knowledge about PUR ageing as found in museum collections.

Optical microscopy highlighted important physical changes throughout the ageing process of polyurethane foams, films and fibres; and infrared spectroscopy highlighted the importance of monitoring the carbonyl region as a main spectral line to follow ageing and changes in hydrogen-bonding interactions. As these secondary interactions play a significant role in the design and preservation of the foam physical properties, their monitoring has been proved to be of fundamental importance in the understanding of changes in PUR supramolecular structure upon ageing. Furthermore, since the C=O stretching absorption from urea (at c. 1640 cm^{-1}) has been identified as an indicator of the ordered structure of PUR HS domain in polymerisation studies, this band was monitored in this research upon ageing experiments. This monitoring suggested significant modifications in hydrogen-bonding interactions between HS chains in PURs, and the possible disintegration of PUR segregated structure over ageing. In cases where PUR does not show this band at t=0 (such as in the selected TPUs), both the C–N stretching and N–H bending, and the C–O–C bands from the urethane linkage have been used (at c. 1225 and 1175 cm^{-1}, respectively), and confirmed as good markers to follow TPU ageing.

As this chapter is mostly focused on PUR foams, Tables 3.1–3.3 have been designed, summarising the main results of the present research. The results shown in these tables consider PUR foam samples showing whitish colours at t=0. For that reason, coloured samples at t=0 might show different ageing pathways, which could not fall into these results. Overall, based on OM, significant differences have been detected when analysing degraded ether- or ester-based PUR foams. Optical microscopy has also proved to offer the possibility of proposing a condition grade for a PUR (especially foams) without requiring extra analytical methods such as IR or Raman spectroscopy. For example, while in general PUR foams show yellowing and loss of transparency and brightness upon ageing, specific visual damages have been detected when analysing ether- or ester-based foams. Ether-based PUR foams showed a gain of roughness in the cell struts with the formation of micro holes, pitting and cracks; and ester-based PUR foams showed a high gain in viscosity and stickiness, but not the formation of micro holes or pitting. On the other hand, cracks crossing the entire cell struts have been identified in both types. When comparing slabstock and cold-moulded foams (within ether-based PUR foams), IR spectroscopy proved to be more efficient than OM in the distinction of the two production classes. Whereas the visual damages were analogous at the micro level, IR spectroscopy pointed to different molecular ageing behaviours, especially in the carbonyl region. Regarding hydrogen-bonding interactions, their IR spectroscopy assessment has supported what has been stated in the literature, i.e., H-bonds in cold-moulded foams might be more easily disrupted than in slabstock foams.

In sum, OM and IR spectroscopy proved to be highly useful in the assessment of PUR degradation in both references and historical objects, confirming their use as complementary techniques as extremely helpful in the visual and molecular characterisation of PUR ageing.

Table 3.1 General molecular and visual evolution upon ageing of ether-based PUR slabstock foams and correlation with condition grades

Visual changes		**Molecular changes**	
Macro Level (by naked eye)	**Micro Level (by OM)**	**HS domain morphology (by IR spectroscopy)**	**IR spectrum**
Good condition Whitish colour and elastic when handled	Bright whitish colour, transparent and defect less cell struts	Long length and efficiently packed HS domains Strong H-bonds within HS domain	–
Fair condition Slight yellow colour and physical stability when handled	Slight yellowing, loss of transparency and formation of micro holes and outline disruptions in the cell bun shape	Decrease of H-bonds within HS domain	Decrease of ν(C–H), 3000–2850 cm^{-1} Decrease of $\nu(C=O)_{urea}$ at c. 1640 cm^{-1} Decrease of ν(C–O–C) at c. 1100 cm^{-1}
Poor condition Yellow/orange colour and susceptibility to rupture when handled	Yellowing/orange colour, loss of transparency, development of micro cracks and ruptures on the PUR foam cell bun	Decrease of H-bonds within HS domain Disordering of the HS domain	Slight spectral changes in ν(N–H), 3700–3200 cm^{-1} High decrease of ν(C–H), 3000–2850 cm^{-1} Higher shift of $\nu(C=O)_{urea}$ at c. 1640 cm^{-1} to higher wavenumbers High decrease of ν(C–O–C) at c. 1100 cm^{-1}
Unacceptable condition Yellow/brown colours and high level of crumbling	Intense yellowing/brown colour, complete loss of transparency, cell bun embrittlement, formation of cracks completely crossing the cell strut, appearance of pitting and slight release of a viscous residue when handled	Plasticisation of HS chains within the HS domain Formation of H-bonds within HS domain with water molecules and/or radicals formed	Increase of ν(O–H), 3750–3400 cm^{-1} Shift of ν(N–H) at c. 3300 cm^{-1} to lower wavenumbers or increase of ν(N–H), 3700–3200 cm^{-1} Higher decrease of ν(C–H), 3000–2850 cm^{-1} Shift of $\nu(C=O)_{urea}$ at c. 1670 cm^{-1} to c. 1640 cm^{-1} and significant increase of the band Increase of $\nu(C=O)_{urethane}$ at c. 1725 cm^{-1} Very high decrease of ν(C–O–C), at c. 1100 cm^{-1}

Table 3.2 General molecular and visual evolution upon ageing of ether-based PUR cold-moulded foams and correlation with condition grades

Visual changes		**Molecular changes**	
Macro Level (by naked eye)	**Micro Level (by OM)**	**HS domain morphology (by IR spectroscopy)**	**IR spectrum**
Good condition Whitish colour and elastic when handled	Bright and defect less cell struts	Short length and weakly ordered HS domains Weak H-bonds within HS domain	–
Fair condition Slight yellow colour and physical stability when handled	Yellowing and formation of micro holes and outline disruptions in the cell bun shape	Decrease of H-bonds within HS domain Disordering of the HS domain	Slight spectral changes in ν(N–H), 3700–3200 cm^{-1} Decrease of ν(C–H), 3000–2850 cm^{-1} Small increase of both $\nu(C=O)_{urethane/urea}$ at c. 1710 cm^{-1} and $\nu(C=O)_{urea}$ at c. 1660 cm^{-1} Decrease of ν(C–O–C) at c. 1100 cm^{-1}
Poor condition Yellow/orange colour and susceptibility to rupture when handled	Yellowing, cell bun embrittlement, development of micro cracks and ruptures on the PUR foam cell bun	Decrease of H-bonds within HS domain Disordering of the HS domain	Shift of ν(N–H) at c. 3300 to lower wavenumbers Decrease of ν(C–H), 3000–2850 cm^{-1} Increase of both $\nu(C=O)_{urethane/urea}$ at c. 1710 cm^{-1} and $\nu(C=O)_{urea}$ at c. 1660 cm^{-1} Decrease of ν(C–O–C) at c. 1100 cm^{-1}
Unacceptable condition Yellow/brown colours, fragile network, complete loss of elasticity and high level of crumbling	Intense yellowing, large-scale cell bun embrittlement, formation of cracks completely crossing the cell strut, complete collapse of the foam	Complete disordering of the HS domain	Increase of ν(N–H), 3700–3200 cm^{-1} Higher decrease of ν(C–H), 3000–2850 cm^{-1} Broadening and increase of $\nu(C=O)_{urethane}$ at c. 1720 cm^{-1} Higher decrease of ν(C–O–C) at c. 1100 cm^{-1}

Table 3.3 General molecular and visual evolution upon ageing of ester-based PUR slabstock foams and correlation with condition grades

Visual changes		Molecular changes	
Macro Level (by naked eye)	**Micro Level (by OM)**	**HS domain morphology (by IR spectroscopy)**	**IR spectrum**
Good condition Whitish colour and elastic when handled	Bright whitish colour, transparent and defect less cell struts	Long length and efficiently packed HS domains Strong H-bonds within HS domain	–
Fair condition Slight yellow colour and physical stability when handled	Bright and defect less surfaces, slight yellowing and loss of transparency	Decrease of H-bonds within HS domain	Decrease and shift of ν(N–H) at c. 3320 cm^{-1} to higher wavenumbers Decrease of ν(C–H), 3000–2850 cm^{-1} Decrease of $\nu(C=O)_{ester}$ at c. 1730 cm^{-1} and decrease and shift of $\nu(C=O)_{urea}$ at c. 1640 cm^{-1} to higher wavenumbers Small decrease of both $\nu(C–O–C)_{ester}$ at 1180 cm^{-1} and $\nu(O–C–H_2)$ at 1134 cm^{-1}
Poor condition Yellow/orange colour, stickiness and susceptibility to rupture when handled	Bright and defect less surfaces, yellowing/orange colour, loss of transparency, viscosity when handled	Decrease of H-bonds within HS domain Disordering of the HS domain	Increase and shift of ν(N–H) at c. 3320 to lower wavenumbers Decrease of ν(C-H), 3000–2850 cm^{-1} Decrease of $\nu(C=O)_{ester}$ at c. 1730 cm^{-1} and decrease and shift of $\nu(C=O)_{urea}$ at c. 1655 cm^{-1} to lower wavenumbers Decrease of both $\nu(C–O–C)_{ester}$ at 1180 cm^{-1} and $\nu(O–C–H_2)$ at 1134 cm^{-1}
Unacceptable condition Yellow/brown colours, high level of crumbling, high stickiness and presence of white crystals	Intense yellowing/brown colour, complete loss of transparency, formation of cracks completely crossing the cell strut, appearance of adipic acid (white crystals), highly viscous, sticky and formation of clumps with minor manipulation of the cell bun	High plasticisation of HS chains within the HS domain Formation of H-bonds within HS domain with water molecules and/or radicals formed	High increase of ν(N–H) between 3700–3200 cm^{-1}, centred at c. 3290 cm^{-1} Higher decrease of ν(C–H), 3000–2850 cm^{-1} High decrease of both $\nu(C=O)_{ester}$ at c. 1735 cm^{-1} and $\nu(C=O)_{urethane}$ at c. 1712 cm^{-1} Shift of $\nu(C=O)_{urea}$ at c. 1655 cm^{-1} to c. 1640 cm^{-1} and significant increase of the band at this wavenumber High decrease of ν(C–N) and δ(N–H) at 1225 cm^{-1} High decrease of of both $\nu(C–O–C)_{ester}$ at 1180 cm^{-1} and $\nu(O–C–H_2)$ at 1134 cm^{-1}

CHAPTER 4

CONSERVATION STUDIES FOR POLYURETHANE

Part of the content of this chapter has already been published:

França de Sá, S., Ferreira, J. L., Matos, A. S., Macedo, R., Ramos, A. M. 2016. A new insight into polyurethane foam deterioration – the use of Raman microscopy for the evaluation of long-term storage conditions. *Journal of Raman Spectroscopy*, 47(12): 1397–1565. DOI 10.1002/jrs.4984.

França de Sá, S., Ramos, A. M., Macedo, R., Ferreira, J. L., Coutinho, B. 2014. How to keep what was intended to be temporarily functional? Reflections on decision-making for the conservation of polyurethane ready-to-wear fashion. In: R. Gordon, E. Hermens and F. Lennard, eds. *Authenticity and Replication: the 'real thing' in art and art conservation*. London: Archetype Publications, pp. 193–203. ISBN 978-1-904982-99-9.

4.1. Preamble

As discussed in Chapter 1, there is no systematic research for the definition of storage conditions for PUR, even though this is one of the most difficult synthetic polymers to preserve. With a lifespan of 20–50 years, many PUR-based objects show severe deterioration signs, which, so far, cannot be prevented. With the attempt to fill this gap in the current knowledge, this chapter aims at bringing new contributions for lowering PUR slabstock foams and TPU films/coatings deterioration rate. For that, different storage conditions have been selected and studied through an ageing experiment. According to S. Michalski, materials 'that suffer from inherent chemical decay can be assumed to last approximately twice as long for each 5°C drop in storage temperature' (Michalski, 2002: 70). In addition, light and oxygen have been generally identified as the main causes of ether-based PUR deterioration (van Oosten, 2011), whereas moisture and temperature have been identified as degradation sources for ester-based PUR deterioration (Lattuati-Derrieux *et al*., 2011). For those reasons, anoxic and low T (≈12°C) conditions have been selected as promising preventive measures for the long-term storage of PUR (both in the dark and at 45–55% RH). For the selection of the T value (≈12°C), the statement of S. Michalski was taken into consideration as well as the research work conducted by Y. Shashoua that focused on low T storage for plastics such as PVC. As stated by Shashoua, 'Although it is widely accepted that reducing the storage temperature of plastics materials inhibits rates of chemical degradation, the influence of reducing the temperature on their physical degradation has not been examined in detail' (Shashoua, 2004: 91). For this reason, there is a 'limited practical experience of its effects in real time' (Shashoua, 2009b: 203). The selection of a specific T range was thoroughly discussed for the design of this experiment. In accordance with Shashoua, the T difference from one environment to another should not surpass 6°C–10°C to avoid condensation (Shashoua, 2014). Consequently, decreasing the T to a maximum of c. 10°C was the chosen compromise for the ageing experiment discussed here. By selecting a T close to 12°C (c. 10°C less than room temperature), it might be possible to benefit from a slower rate of deterioration (as proposed by Michalski), to minimise possible physical damages to the material (such as shrinkage or stiffening) and to avoid condensation. Besides this selection, the range of RH was also discussed. Although lower values of RH (≈30%) would be advantageous for the preservation of PUR (especially the ester-type), PUR polymers are commonly found in composite objects. In complex museum collections, such as MUDE, a large percentage of PUR-based objects show wood and/or fibres (among other materials) in their composition. For that reason, lower or higher values of RH could have a damaging effect since it may cause physical tensions (e.g. shrinkage). Thus, 45–55% RH was selected as a good preservation compromise for this ageing experiment. To assess the selected storage conditions, a natural ageing experiment in the dark (12 months, 45–55% RH) has been carried out for four selected environments:

open air at room T, and sealed enclosures at room T (with/without oxygen) and low T (11–13°C). To extend the validation of the results, both unaged (model PUR foams and TPU film) and naturally pre-aged references (produced 8–10 years ago) were included. This allows verifying if the selected storage conditions are beneficial for the preservation of unaged objects but also historical assets. For the ageing assessment, gravimetry (weight measurements), colourimetry, stereomicroscopy, OM (visible and UV light), IR and Raman μ-spectroscopies were selected. Contact angle (°) and hardness (Shore A) measurements were also carried out for the exclusive assessment of TPU films upon ageing. Although vital information on PUR deterioration has been commonly provided by IR spectroscopy (as mentioned in Chapter 1), Raman microscopy was also included because several authors have mentioned that this technique is a valuable tool for the characterisation of important features in PUR complex structure. For instance, Raman spectroscopy was successfully used for the characterisation of domain structures and phase behaviour of copolyurethanes (Hu *et al*., 1992), of hydrogen-bonding interactions on different polyurethane-urea films (Romanova *et al*., 2002), and of hydrogen-bonding interactions on different mole fractions of hard-to-soft segments in a TPU (Weakley *et al*., 2012). Moreover, Sassi *et al*. and Venkataramani *et al*. have mentioned that IR spectroscopy is not as sensitive to amide I side chain environments as Raman spectroscopy (Sassi *et al*., 2011 and Venkataramani *et al*., 2013 apud Lewis *et al*., 2014). With the prior knowledge that: (i) 'polyurethanes are strongly self-associated through intermolecular hydrogen bonding' (Coleman, 1988: 60); (ii) these bonds are labile to moisture and temperature; (iii) natural ageing processes may result in severe modifications of PUR segregated morphology through the deterioration of its secondary bonds (as suggested in Chapter 3); and that (iv) the ageing experiment in this chapter was carried out in standard storage conditions for one year (i.e. small scale ageing was expected), the use of Raman microscopy was selected in order to enable the detection of early stages of molecular deterioration and to complement the information obtained by IR spectroscopy. Promising results were obtained and the definition of the optimum storage conditions for the preservation of PUR foams and TPU films/coatings can be launched.

This chapter also discusses, from a theoretical point of view, conservation and curatorial strategies defined for contemporary ready-to-wear fashion and product design objects containing PUR and already showing degradation (due to the presence of this polymer). It aims at contributing to the awareness of difficult decision-making processes involved in the preservation of PUR-based objects from museum collections and to discuss whether new paradigms could be set. As the rate of PUR degradation is high, in some cases, relatively new objects start to degrade before any decision about their preservation is made. To highlight the lack of time sometimes involved in such cases, degraded PUR-based objects from the MUDE collection dated between 1999–2007 are discussed. As the presence of PUR was the cause of their short-term degradation (after some months in display), these objects reflect how fast PUR degradation process can be and how, in some cases, conservators do not

have time to predict ageing and establish preventive measures. Therefore, this chapter presents a brief discussion about this subject by looking at concepts such as authenticity, replication, replacement and original materiality, and by surveying conservation strategies already practiced by museums holding similar collections as MUDE (see Appendix II for more information on the questionnaires and surveys).

4.2. Dark ageing study for the assessment of selected storage conditions

4.2.1 Methodology

A natural ageing experiment in the dark was carried out for the study of selected storage conditions for PUR. In this study, ether- and ester-based PUR slabstock foams and ester-based TPU films were included (Fig. 4.1).

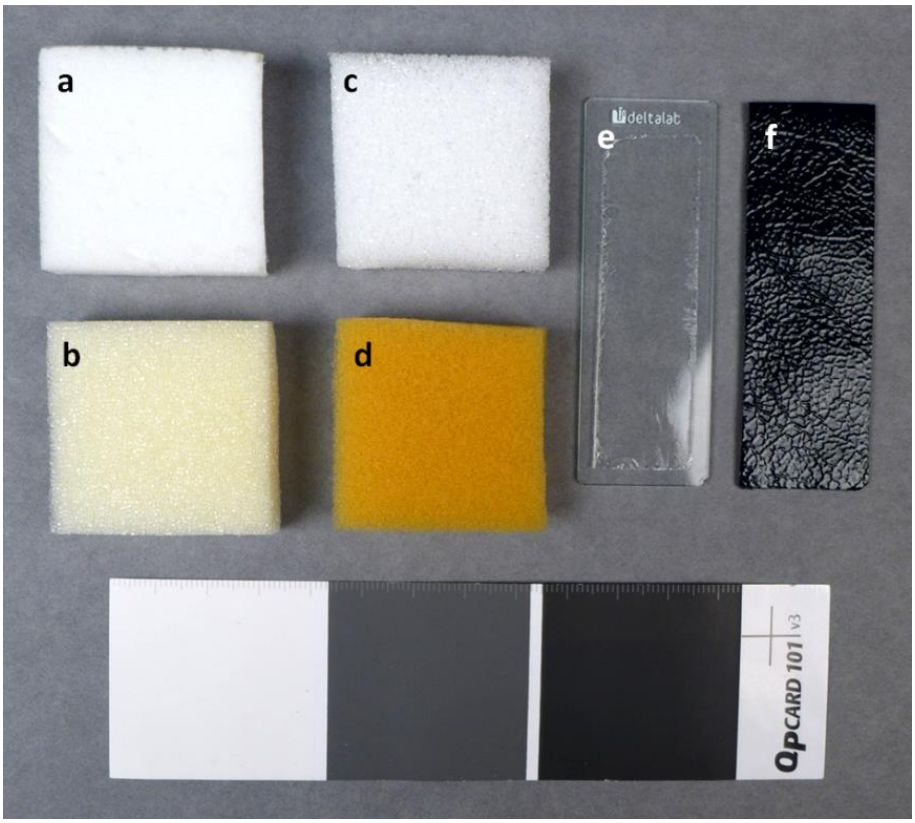


Figure 4.1 Reference samples included in the natural ageing experiment in the dark: unaged (a) and naturally pre-aged (b) ester-based PUR slabstock foam; unaged (c) and naturally pre-aged (d) ether-based PUR slabstock foam and unaged (e) and naturally pre-aged (f) ester-based TPU film.

For each type (ether and ester) and form (foam and film) of PUR, two references were selected with the aim to include samples showing different conditions: an unaged reference (good condition) and a naturally pre-aged reference (fair or poor conditions) (Fig. 4.1). The chemical and visual characteristics

of the unaged references are discussed in sections 3.3.1.1 and 3.4.1.1 (see also Appendix I). The main characteristics of the naturally pre-aged reference are shown in Appendix I.
The samples were submitted to an ageing experiment in the dark at 45–55% RH during 12 months. The remaining variables followed the subsequent specifications for each condition[100]:

(i) open-air storage - samples in open-air, at room T;
(ii) enclosed storage – samples in sealed enclosures without oxygen removal, at room T;
(iii) cool-enclosed storage[101] – samples in sealed enclosures without oxygen removal, at c. 12°C;
(iv) anoxic storage – samples in sealed enclosures with oxygen removal, at room T.

For the sealed enclosures, each sample was placed inside combined bags made of one-side ESCAL (transparent film side) and one-side aluminium barrier films (opaque side) (see properties in Appendix I). Depending on the storage condition, additional items were added on the enclosures. Humidity indicator cards from SÜD-Chemie Performance Packaging were used for the monitoring of RH inside the low T enclosures (see properties in Appendix I) and oxygen indicators and scavengers RP-K from Mitsubishi Gas Chemical were included in the anoxic enclosure (see properties in Appendix I). For each storage condition, open containers (8 x 8 x 2.5 cm) of polyester film from Melinex® were produced to prevent any direct contact between samples and packaging materials.
Five independent specimens per each storage condition and per PUR type were collected for periodic assessment. The assessment was carried out by stereomicroscopy, OM (under visible and UV light), gravimetry, colourimetry, IR μ-spectroscopy (transmission mode) and Raman spectroscopy after one, three, six, nine and twelve months (see Appendix I). For TPU films, contact angle (°) and hardness (Shore A) measurements were also included. Further statistical treatment was carried out based on the one-way analysis of variance (ANOVA), followed by the Post-Hoc Tukey-Kramer multiple comparison test in order to identify significant differences (*p*-value below 0.05) (see Appendix I for more details). Each sample was analysed in three independent areas.
In total, 150 samples were included in the ageing experiment and 120 samples were analysed. The last group of samples (30 samples) remains in each storage condition to enable the evaluation of their efficiency and efficacy in the long-term preservation of PUR and to extend the obtained results.

[100] Hereinafter, the underlined designations will be used to define the storage condition in discussion.
[101] The term 'cool-enclosed storage' was adopted according to the definition provided by the *Image Permanence Institute*, i.e. 'A storage condition with temperatures usually between 45°F (7°C) and 60°F (16°C)' (Image Permanence Institute, 2017).

4.2.2 Ether-based PUR slabstock foams

Since both ether-based references showed similar results upon the natural ageing experiment, only the data concerning the model PUR (unaged reference) are discussed in detail. For the naturally pre-aged reference only main conclusions are highlighted.

4.2.2.1 Ether-based PUR foam references characterisation

The visual and molecular (based on IR spectroscopy) insight of the unaged model was already provided in Chapter 3 (section 3.3.1.1); therefore, only main differences regarding the naturally pre-aged reference (commercial sample) are discussed here. While the good condition of the unaged model is evidenced by the bright whitish colour and defectless cell struts (Fig. 3.1); the poor condition of the naturally pre-aged commercial sample is evident by the yellow colour of the cell buns and presence of micro holes (Figs. 4.1 and 4.2). Similarly to previous cases (see Chapter 3), these foams show fluorescence under longer (blue-violet light) and shorter (ultraviolet light) wavelengths. The unaged reference shows a weaker fluorescence intensity (Fig. 3.1) when compared to the commercial sample, previously aged for ten years (Fig. 4.2)[102].

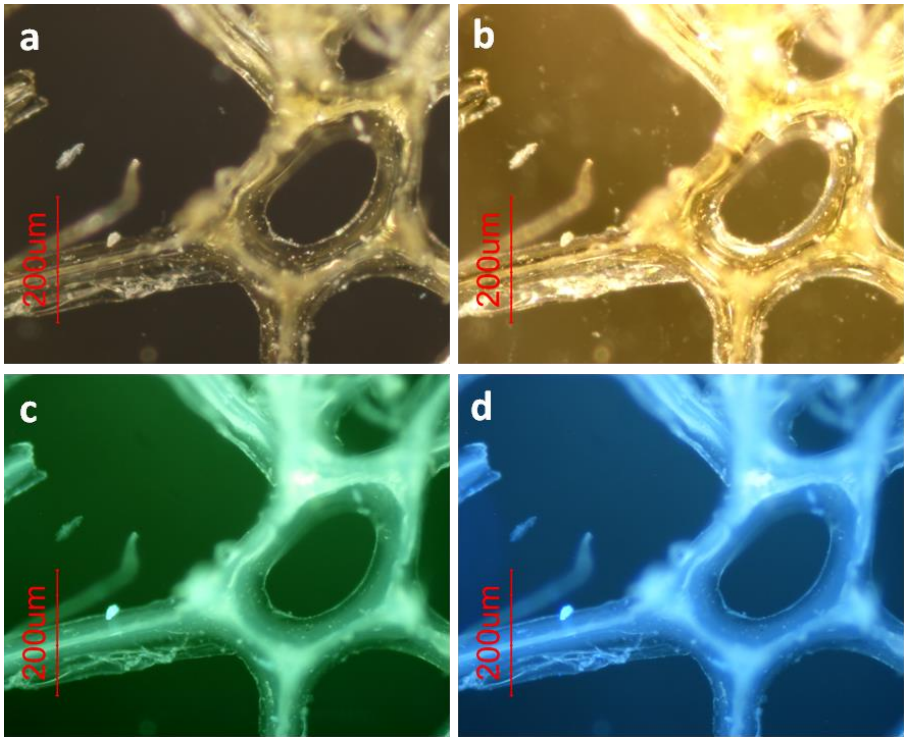


Figure 4.2 Microscopy images of the naturally pre-aged ether-based PUR foam under cross-polarised light (a), darkfield (b), blue-violet light (c) and ultraviolet light (d).

[102] The molecular groups possibly responsible for this behaviour are discussed in Chapter 3.

From IR spectroscopy and according to the literature, both unaged and commercial references spectra show the characteristic bands of water-blown polyether-based polyurethane slabstock foams (Fig. 4.3) (Priester *et al*., 1990; Elwell *et al*., 1996; Wilhelm & Gardette, 1998; Wilhelm *et al*., 1998). However, significant spectral differences can be observed between the two, which result from their different condition. From the unaged to the naturally pre-aged foam there is a significant decrease of the absorption bands between 2970–2867 cm^{-1} (C-H stretching region), at 1107 cm^{-1} (stretching vibration of C–O–C groups) and at 1727 cm^{-1} ($C=O_{urethane}$ stretching, free of hydrogen-bonding). Along with these changes, the band at 1643 cm^{-1} ($C=O_{urea}$ stretching, bidentate urea) shifts to higher frequencies. This may indicate the loss of strong hydrogen-bonding interactions between HS chains as well as the poor resistance of ether-based SS to environmental conditions, probably imposed by the unprotected storage of the foam plate during the last 10 years (see more information in Appendix I).

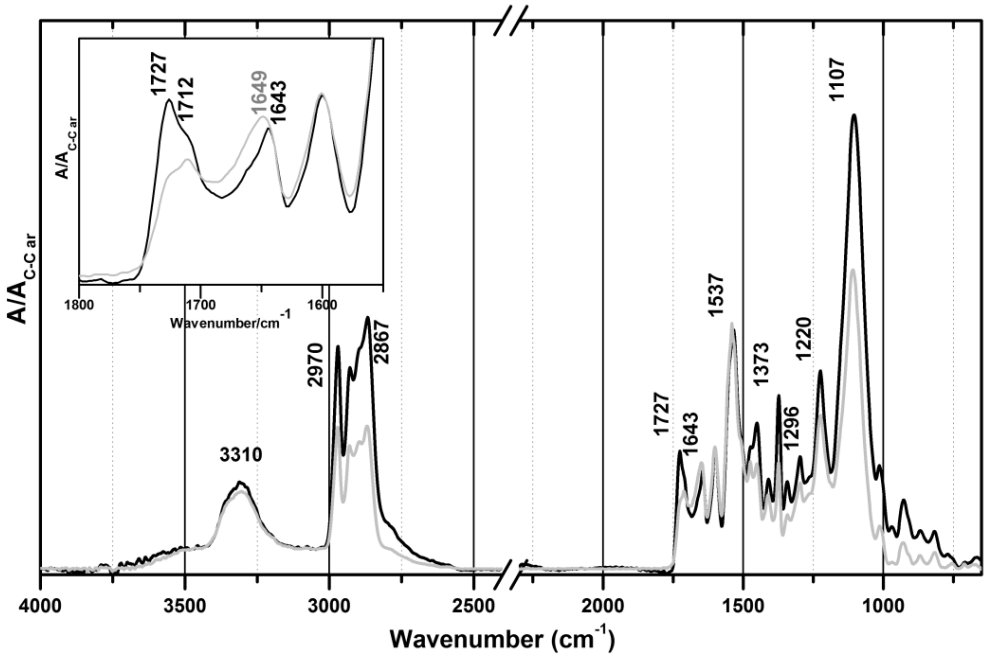


Figure 4.3 Infrared spectra of the unaged and naturally pre-aged ether-based PUR foams. Inset: Detail of the carbonyl region from 1800 to 1550 cm^{-1}.

From Raman spectroscopy, complementary information was obtained. Tentative band assignments are made from reference to earlier Raman studies on model TPUs (Miller *et al*., 1990; Hu *et al*., 1992; Romanova *et al*., 2002; Janik *et al*., 2003; Parnell *et al*., 2003; Bruckmoser & Resch, 2014 and citations therein). As expected, the most intense bands from the Raman spectra are assigned to C–C, C=C, C–N and N–H groups (Figs. 4.4 and 4.5). Therefore, Raman microscopy provided further information about the polymer network of the PUR in study. Since important results were achieved and Raman

spectroscopy on PUR foams is not commonly explored, each full spectrum is shown separately and the C=C and C=O stretching regions are shown overlaid, in detail (Fig. 4.6).

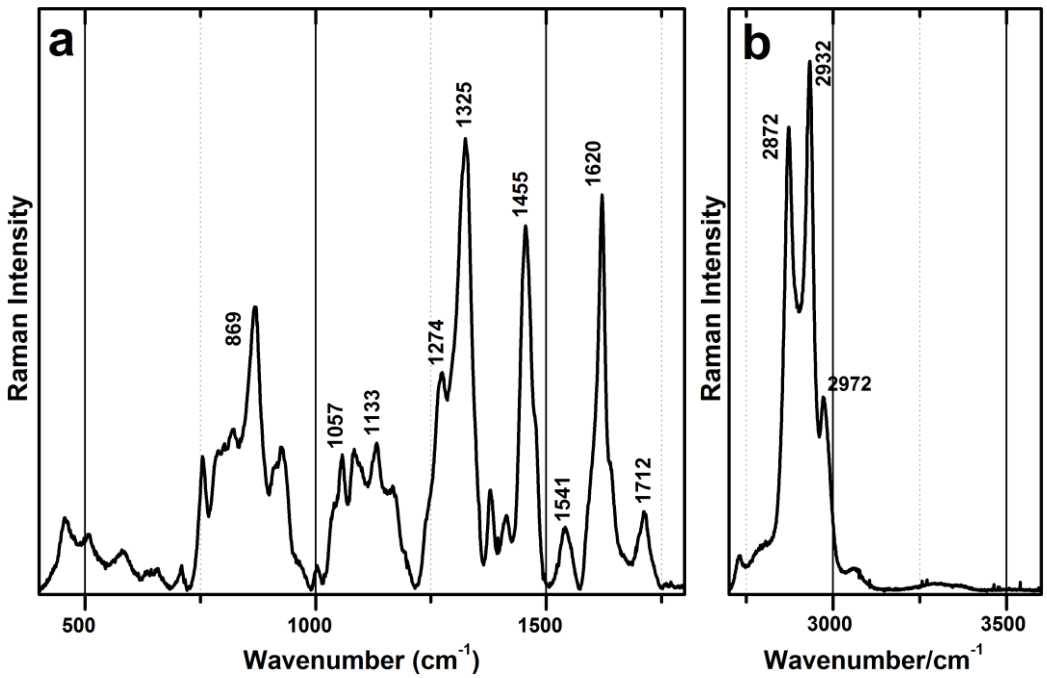


Figure 4.4 Raman spectra of the unaged ether-based PUR foam from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

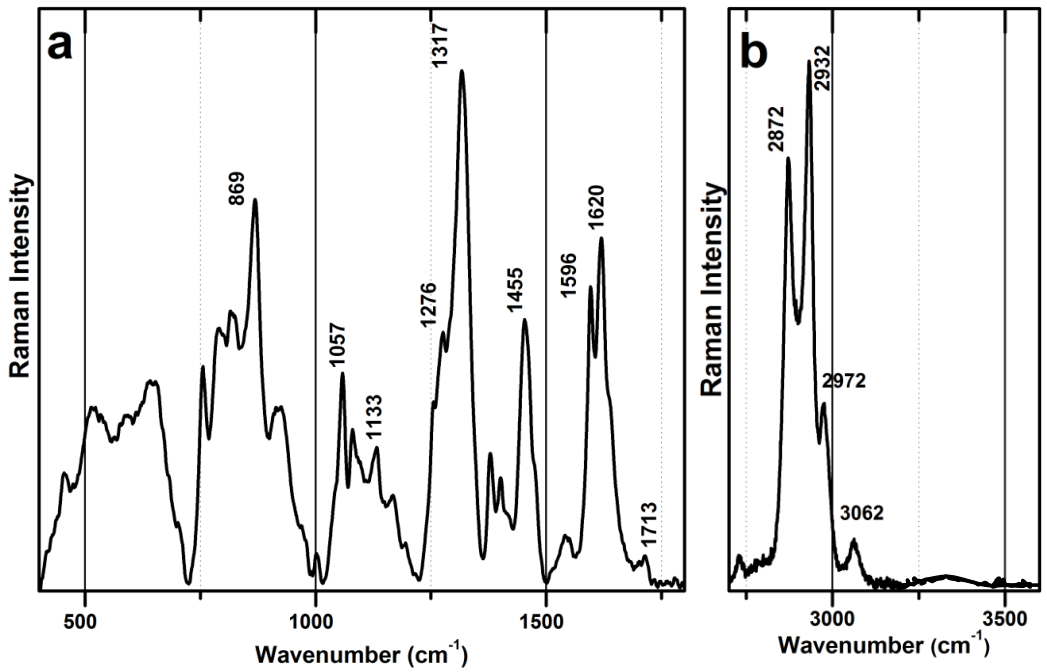


Figure 4.5 Raman spectra of the naturally pre-aged ether-based PUR foam from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

Regarding the assignment of the most important bands in both spectra (Figs. 4.4 and 4.5), the ether-based SS is confirmed by the complex bands between 1000–1200 cm^{-1} (C–O stretching) as well as by the bands at 1455 cm^{-1} (C–H_2 bending), 2872 and 2932 cm^{-1} (C–H_2 stretching) and 2972 cm^{-1} (C–H_3 stretching). The HS is characterised by the bands at 1274 cm^{-1} (C–N stretching and N–H bending in amide III), 1325 cm^{-1} (C–H_2 wag/twist), 1541 cm^{-1} (C–N stretching and N–H bending in amide II), 1620 cm^{-1} (C=C stretching from aromatic ring), by the carbonyl bands at c. 1660 cm^{-1} (shoulder), 1700 cm^{-1} (shoulder) and 1712 cm^{-1} (C=O stretching wavenumbers), and by the bands at 3060 cm^{-1} (C–H stretching from the aromatic ring) and between 3175–3412 cm^{-1} (N–H stretching). In addition, several differences can be detected between the two spectra, especially in the C=C and C=O stretching regions, which could be related to the different conditions of the foams (Fig. 4.6).

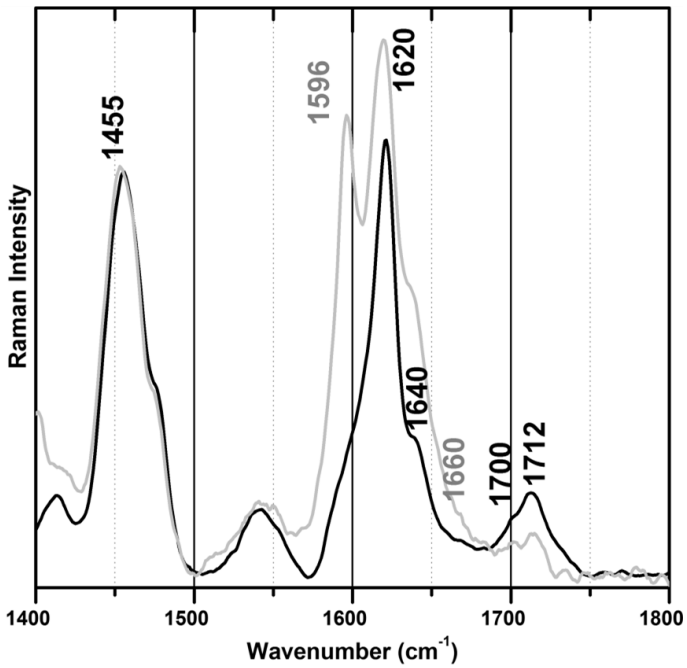


Figure 4.6 Raman spectra of the unaged (black) and naturally pre-aged (grey) ether-based PUR foam from 1400 to 1800 cm^{-1}.

As shown, there is a broadening of the band centred at 1620 cm^{-1} (C=C stretching from aromatic ring), the appearance of a band at 1596 cm^{-1} (doublet C=C stretching from the aromatic ring, along with the band at 1620 cm^{-1} or, C=C stretching from formation of polyenes) (Edwards, 2002) and the decrease of the bands relative intensities at 1700 and 1713 cm^{-1} (C=O stretching). The increase of the band at 3062 cm^{-1} is also observed, previously assigned to C–H stretching from the aromatic ring. The

differences observed in the C=C stretching bands[103] may explain the strong orange colour of the naturally pre-aged reference (increase of conjugated double bonds due to the foam exposure to oxygen and light (possibly) over the last 10 years). Another difference was the broad underlying interference caused by fluorescence during the collection of spectra from the naturally pre-aged samples. This has resulted in spectra showing higher noise and bands with lower resolution, especially between 400–1000 cm^{-1}.

Regarding the characterisation of hydrogen-bonding, both N-H and in particular C=O stretching wavenumbers reflect these interactions (Fig. 4.6). According to Weakley *et al*., specific bands between 1640–1800 cm^{-1} are able to reveal different microstructures (amorphous, semicrystalline and ordered crystalline) on polymers such as polyamides and polyurethanes (Weakley *et al*., 2012). In the current study, the carbonyl stretching band at c. 1660 cm^{-1} may correspond to H-bonded C=O groups from urea linkages; and the carbonyl stretching wavenumbers at 1700 and 1712 cm^{-1} to H-bonded C=O from urethane linkages with possible different lengths, shorter (1700 cm^{-1}) and longer (1712 cm^{-1}) or to H-bonded C=O groups from urethane linkages in ordered (1700 cm^{-1}) and disordered (1712 cm^{-1}) regions of the PUR segregated morphology (Fig. 4.6). The N–H stretching band between 3175–3412 cm^{-1} may correspond to N-H groups from urea and/or urethane linkages associated through H-bonds (Figs. 4.4 and 4.5). Since the naturally pre-aged samples show the decrease of both C=O stretching bands at 1700 and 1712 cm^{-1}, this may explain its fragile foam network when handled, i.e., the disruption of hydrogen-bonding interactions. However, these hypotheses are only posed based on studies concerning urethane-based thermoplastic elastomers (TPU). Therefore, further research on ether-based PUR foams should be carried out to confirm them.

4.2.2.2 Assessment of the dark ageing experiment

From the gravimetry assessment upon ageing, no relevant results and no tendency were obtained (weight variations below 0.7%) (see Appendix V.1 and V.2).

From the stereomicroscopy images of the unaged model upon 12 months in the dark (Fig. 4.7), two storage groups are clearly distinguishable by the naked eye based on colour assessment, open-air and enclosed systems. The open-air storage led to severe colour changes after one month in the dark, while the enclosed systems prevented discoloration even after twelve months.

[103] The differences associated to the C=O region are explained later in this section, due to their probable relation to changes in hydrogen-bonding interactions.

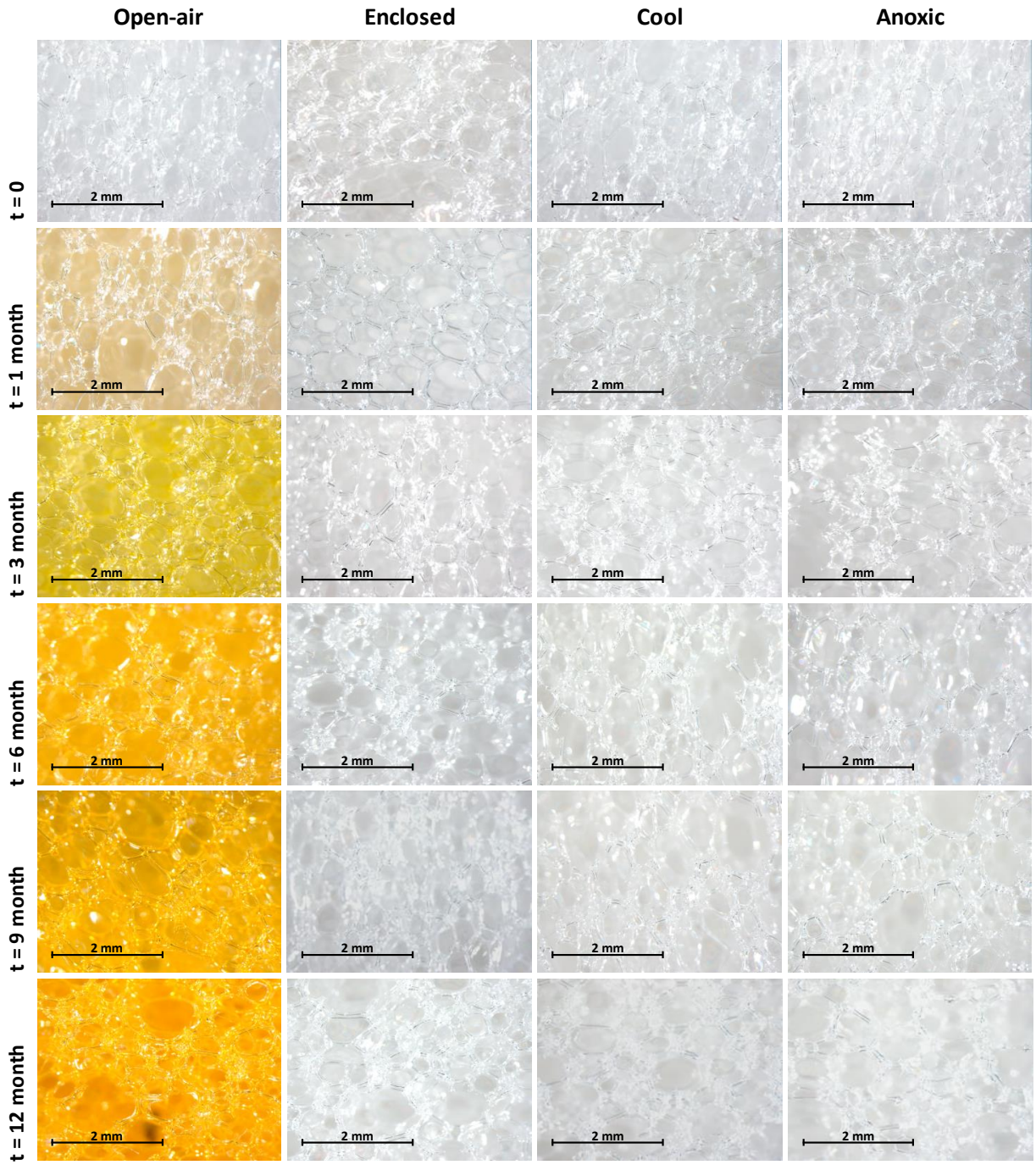


Figure 4.7 Stereomicroscopy images of the unaged ether-based PUR before (t=0) and after ageing (t=[1,12] months) in the dark in different storage conditions. Each image corresponds to a different foam sample.

According to the colourimetric measurements, the unaged model PUR samples in open-air reached total colour variations close to fifteen (ΔE^*>15)[104], already after one month. On the other hand, the samples sealed in barrier film bags did not suffer colour changes, reaching total colour variations slightly above one, even after 12 months.

Concerning the naturally pre-aged reference, comparable results were obtained, although not as drastic due to the yellowing degree of these samples already at t=0. The samples exposed in open-air suffered total colour variations higher than three (ΔE^*≈3.5) after twelve months of ageing, and values below two were obtained for the other storage conditions. Although light has been commonly mentioned as the main cause of ether-based PUR discolouration, based on this first visual approach, it might be possible to attribute the discoloration to the presence and long-term availability of oxygen. Even though the anoxic storage was the only environment where this deterioration agent was lowered to <0.1%, the enclosed systems had oxygen contents around 20% or less, and after their consumption in oxidation reactions, this agent was no longer available for further deterioration. The results published by Shashoua and van Oosten (Shashoua, 2009b; van Oosten, 2011) reporting PUR foams that have suffered yellowing in the dark and open-air are in accordance with this hypothesis. Nevertheless, light ageing experiments in anoxic conditions should also be carried out to highlight the roles of oxygen and light alone in the yellowing of PUR foams. From optical microscopy (conventional light microscopy), since the samples kept in enclosed systems did not suffer any changes clearly visible by this technique, only the images concerning the open-air storage are discussed (Fig. 4.8). In Fig. 4.8, loss of transparency (Fig. 4.8a) and yellowing (Fig. 4.8b) are the most evident ageing consequences affecting these foams. From the fluorescence microscopy images, once more, a gain in fluorescence intensity is observed upon ageing (Fig. 4.8c), which corroborates what has already been stated for the unaged and naturally pre-aged samples. In addition, the unaged PUR emitted different colours upon fluorescence according to ageing exposure periods and yellowing grades, in particular under blue-violet light. This may emphasise the higher sensitivity of the blue-violet wavelengths to the formation of conjugated double bond systems than ultraviolet (Fig. 4.8). In general, the increased fluorescence intensity and colour shifting (here particularly evident) may be associated to the formation of conjugated double bonds and to modifications on the polymer redox state, as previously explained in Chapter 3. From the particular use of optical confocal microscopy (from the Raman equipment), a deeper insight into the superficial changes of the PUR cell struts after 12 months in dark was achieved (Figs. 4.9 and 4.10).

[104] See Appendix I for more details on the colourimetric assessment. Note that ΔE^* values above 2.3 have been considered to correspond to just noticeable differences (JND) (Mahy *et al.*, 1994).

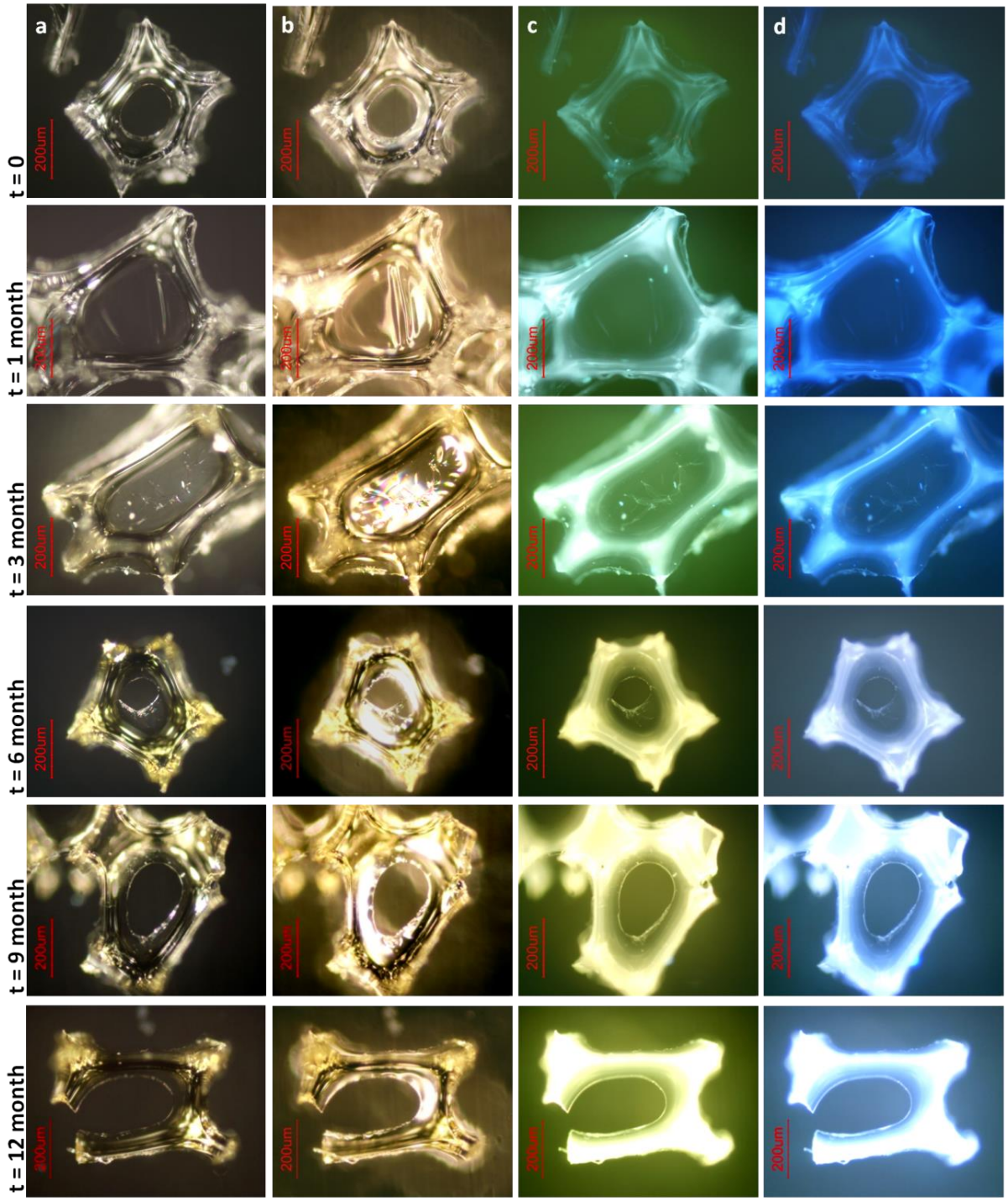


Figure 4.8 Microscopy images of the unaged ether-based PUR foam before (t=0) and after ageing (t=[1,12] months) in open-air: cross polarised light (column a), darkfield (column b), blue-violet light (column c) and ultraviolet light (column d).

According to Robert H. Webb, the use of confocal microscopy results in very high contrast images (Webb, 1996). Given the high depth resolution (which allowed the use of 500x magnification) and the spatial accuracy of this technique, additional and detailed information was collected. As shown in Figs.

4.9 and 4.10, high amplifications of the cell struts superficial image have been possible to assess. The samples stored in open-air after 12 months show a higher level of defects at the surface than the samples stored in the remaining conditions: increased number of micro-holes in the unaged sample (Fig. 4.9d), and increase number of micro holes and cracks in the naturally pre-aged sample (Fig. 4.10d) after 12 months in open-air. From the comparison between the unaged (Fig. 4.9) and the naturally pre-aged (Fig. 4.10) samples, it is also possible to describe micro-holes as one of the first signs of ageing (along with yellowing) in ether-based PUR foams. Based on OM, this has also been observed.

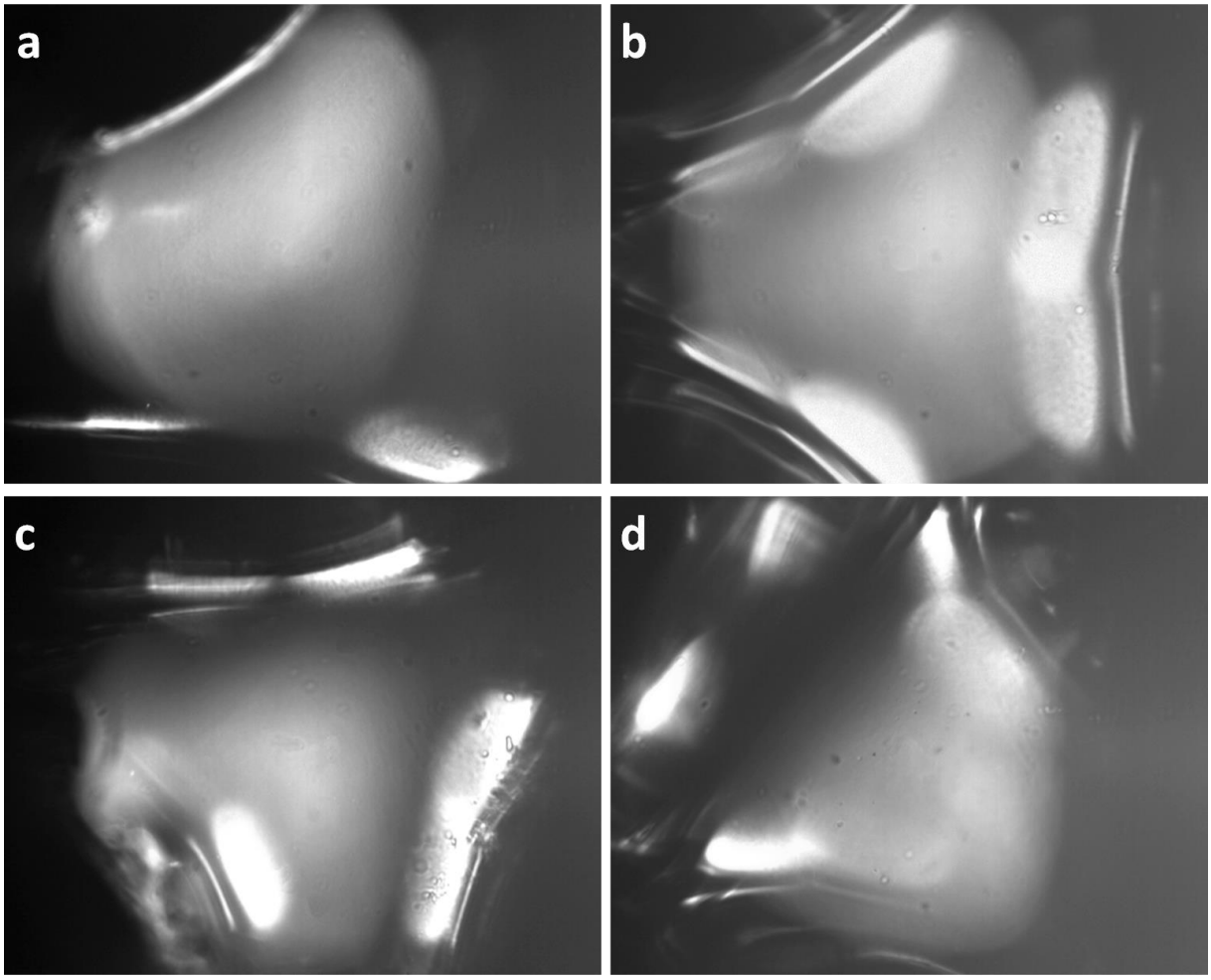


Figure 4.9 Confocal microscopy images (500x) of the unaged ether-based PUR foam cell struts after 12 months in dark ageing at different storage conditions: anoxic (a), cool-enclosed (b), enclosed (c) and open-air (d).

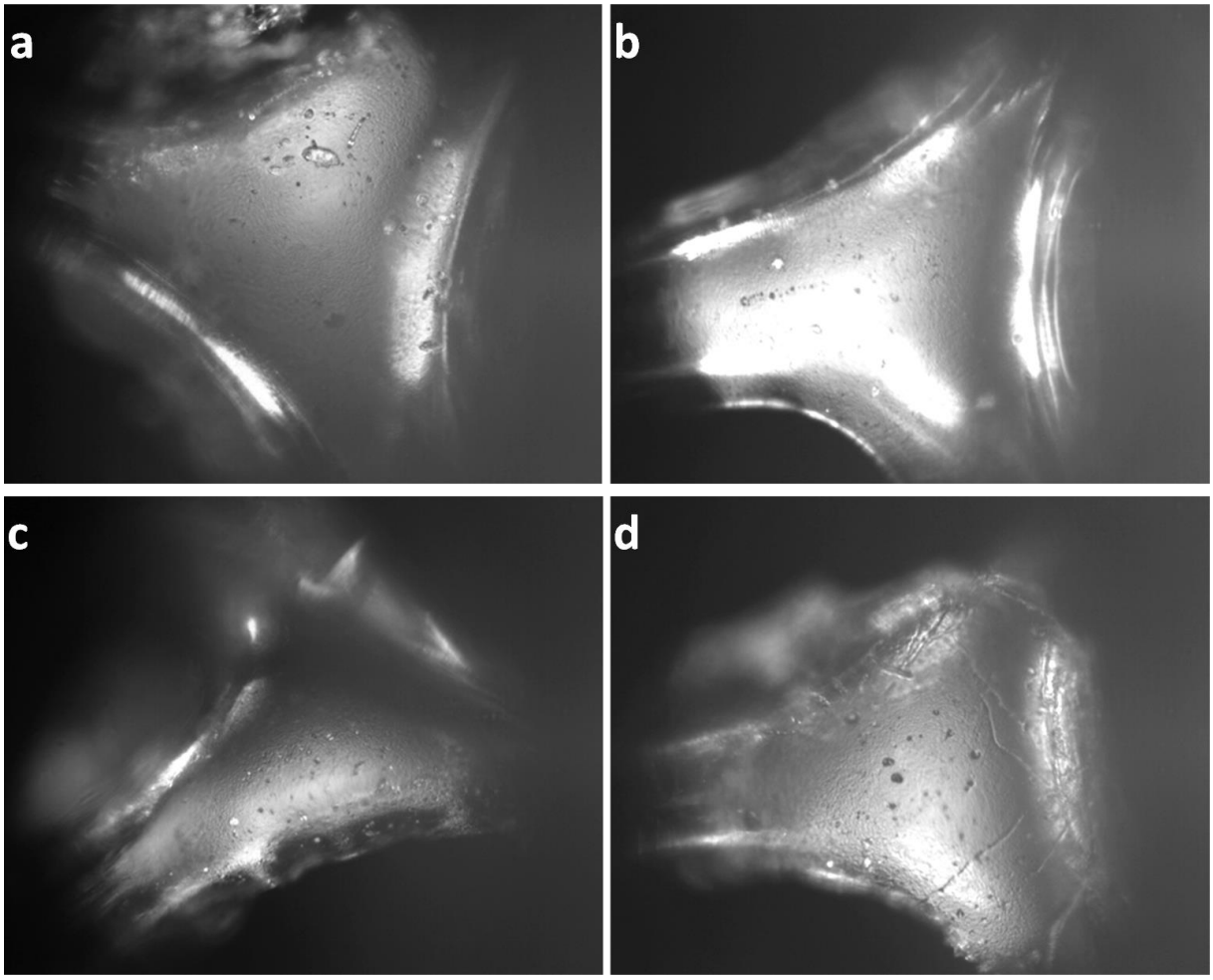


Figure 4.10 Confocal microscopy images (500x) of the naturally pre-aged ether-based PUR foam cell struts after 12 months in dark ageing at different storage conditions: anoxic (a), cool-enclosed (b), enclosed (c) and open-air (d).

From IR spectroscopy it was not possible to distinguish which storage is most suitable (see Appendix V.1 and V.2). This could be attributed to a less sensitivity of the technique, when compared to Raman, to early molecular deterioration stages that are mainly related to yellowing (C=C bonds) (Edwards *et al.*, 1993; Chalmers & Everall, 1999) and minor polymer conformational changes (hydrogen-bonding) (Lewis *et al.*, 2014), and/or to the acquisition method (μ-samples compressed in a diamond anvil cell, transmission mode) that impacts on the relative intensity ratios between bands, especially, the C=O and C–O–C stretching wavenumbers at c. 1643 cm^{-1} and c. 1107 cm^{-1}, respectively. Since the cellular network of the unaged PUR foam is extremely flexible and non-planar, its compression is hindered. In addition, being a natural ageing experiment in the dark (at room or low T and ~50% RH) only small scale deterioration is expected, which together with the extreme sensitivity of the technique to different thicknesses of the material (transmission mode) may have masked possible minor molecular deteriorations. Therefore, the acquisition of reproducible spectra from three independent analyses

has not been possible and no correlations between bands intensity/shift and storage conditions could be clearly established.

On the contrary, based on Raman spectroscopy systematic variations have been identified for both references (unaged and naturally pre-aged) between 1600–1750 cm^{-1}, assigned to C=C and C=O stretching vibrations (Figs. 4.11 and 4.12). Since no reproducible spectral variations were detected on infrared and yellowing was the main ageing consequence (highlighted by colourimetry, stereomicroscopy and OM), Raman microscopy stands out as a promising analytical approach for the translation of minor deteriorations (in this case, yellowing) into clearly discernible spectral lines. These variations were specifically detected at 1620 cm^{-1} (aromatic ring stretching), 1660 cm^{-1} and between 1700–1712 cm^{-1} (carbonyl stretching wavenumbers) (Figs. 4.11 and 4.12) and are expressed as mean and standard deviation values (Figs. 4.13 and 4.14 for the unaged reference; Fig. 4.17 for the naturally pre-aged reference).

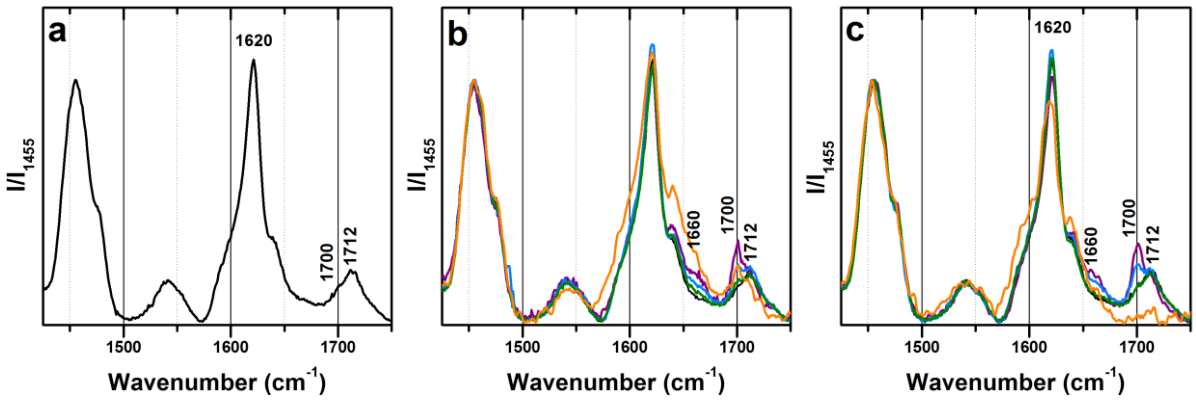


Figure 4.11 Raman spectra of the unaged ether-based PUR foam before (a) and after six (b) and twelve months (c) of natural ageing in the dark from 1425 to 1750 cm^{-1}: open-air storage (orange), enclosed storage (purple), cool-enclosed storage (blue) and anoxic storage (green).

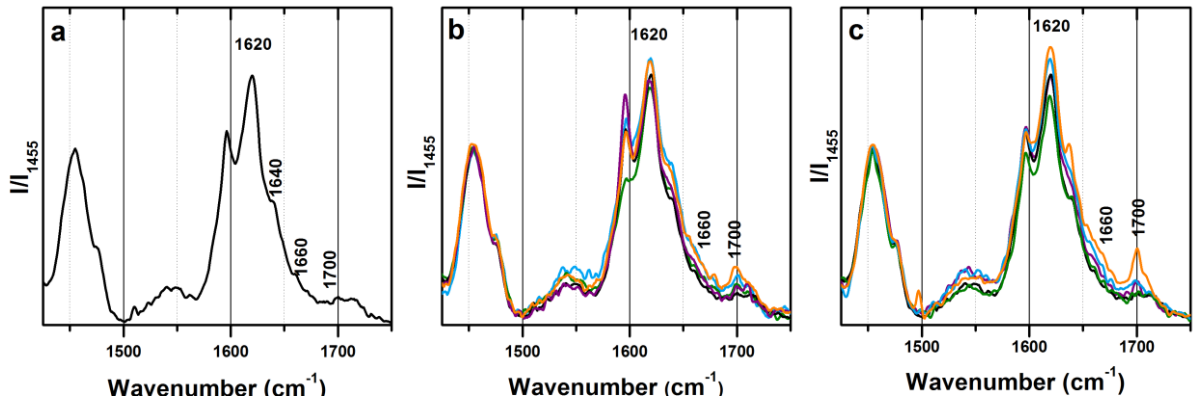


Figure 4.12 Raman spectra of the naturally pre-aged ether-based PUR foam before (a) and after six (b) and twelve months (c) of natural ageing in the dark from 1425 to 1750 cm^{-1}: open-air storage (orange), enclosed storage (purple), cool storage (blue) and anoxic storage (green).

For each wavenumber, the three independent measurements were statistically evaluated by ANOVA Post-Hoc Tukey Kramer multiple comparison test (analysis of variance) to identify significant variations upon exposure: this identification is made with lower case letters and bars with the same letter are not significantly different, and vice versa.

In which concerns the unaged reference, only open-air and enclosed (room T) storage evidenced the existence of significant differences between different ageing periods (time, in months) (Figs. 4.13 and 4.14 – only orange and purple bars show variance with time, which is identified by lowercase letters).

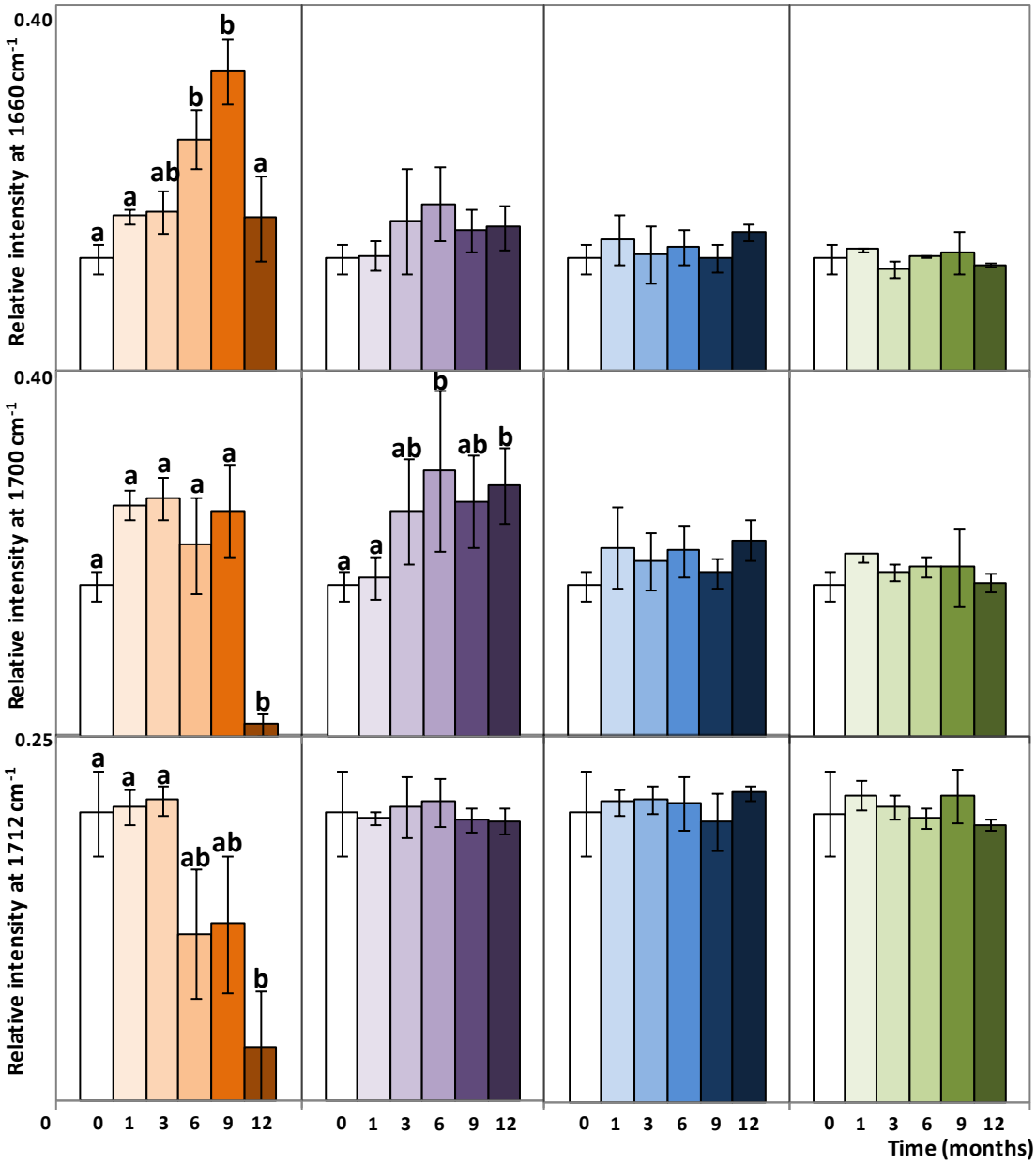


Figure 4.13 Raman intensities normalised for the C–H_2 bending (at 1455 cm^{-1}) of the unaged ether-based PUR foam before (t=0, white bar) and after ageing (t=[1,12] months, colour bars) in different storage conditions: open-air storage (orange bars), enclosed storage (purple bars), cool-enclosed storage (blue bars) and anoxic storage (green bars). All values are means (bar) of triplicates ± SD (whiskers). Statistical significance for ANOVA and

Tukey-Kramer multiple comparison tests was established at a *p*-value < 0.05. Values that are significantly different between times within the same storage are indicated by different lowercase letters.

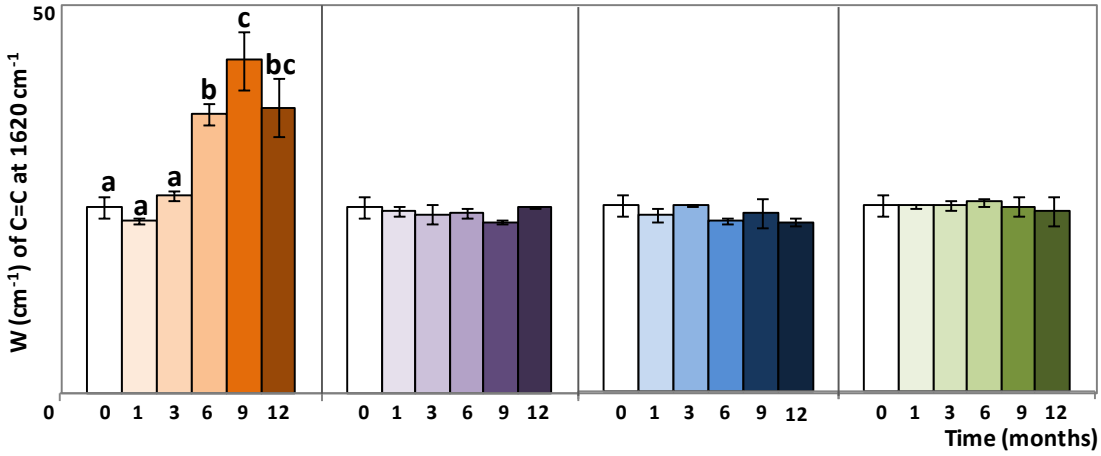


Figure 4.14 Full width at half height (W) of the Raman C=C stretching band at 1620 cm^{-1}, normalised for the C–H_2 bending (at 1455 cm^{-1}) of the unaged ether-based PUR foam before (t=0, white bar) and after ageing (t=[1,12] months, colour bars) in different storage conditions: open-air storage (orange bars), enclosed storage (purple bars), cool-enclosed storage (blue bars) and anoxic storage (green bars). All values are means (bar) of triplicates ± SD (whiskers). Statistical significance for ANOVA and Tukey-Kramer multiple comparison tests was established at a *p*-value < 0.05. Values that are significantly different between times within the same storage condition are indicated by different lowercase letters.

Open-air ageing showed significant variations at all wavenumbers of interest. As an example, along with foam discoloration (Fig. 4.7), broadening of the band at 1620 cm^{-1} is detected (Fig. 4.14). This is possibly explained by the formation of double bonds and conjugated double bond systems which cause foam discolouration, with vibrations at slightly different wavenumbers (Bruckmoser, 2014; Klyachkin *et al*., 1999). In order to correlate the band broadening (W) with the yellowing increase (using the b* coordinate from the CIELab colour space system), the Pearson correlation coefficient was determined. For this case, a positive correlation (0.7001) and a *p*-value of 0.0015 were obtained. This demonstrates that the broadening of the band at 1620 cm^{-1} does reflect the yellowing of the foam and validates the use of Raman spectroscopy for the detection of molecular alterations that lead to yellowing. As shown in Fig. 4.14, the discolouration already observed after one month was only detectable at the molecular level after six months of ageing, with Δb^* values above 45. This may stress that high Δb^* values are required for the detection of new spectral lines as consequence of yellowing.

When both references are compared at both t=0 and t=12 months in open-air (Fig. 4.15), this broadening is also detectable. As the unaged reference showed a white colour at t=0 and a strong orange colour at t=12 months in open-air, the attribution of this band broadening to yellowing gains strength.

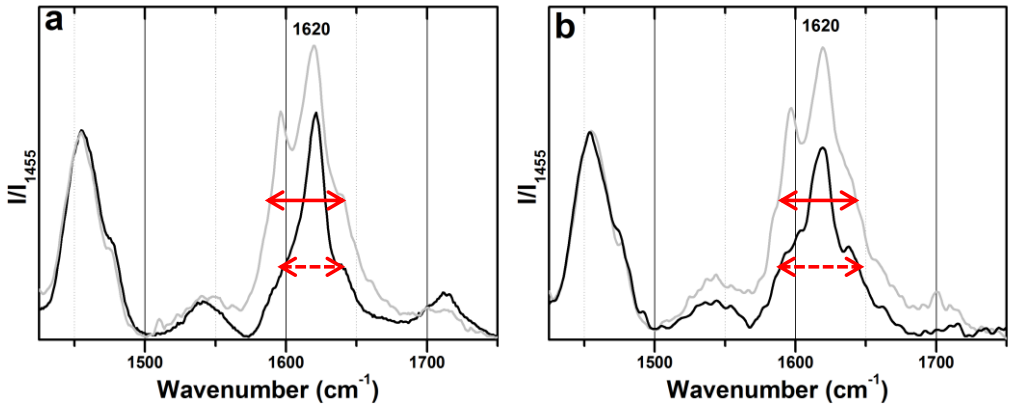


Figure 4.15 Raman spectra of the unaged (black) and naturally pre-aged ether-based PUR foams (grey) before (a) and after twelve (b) months of natural ageing in the dark from 1425 to 1750 cm^{-1} in open-air storage. The red arrows indicate the width at half height of the band centred at 1620 cm^{-1}.

Moreover, both references after t=12 months in open air showed similar colour coordinates, with the exception of the L* coordinate which was higher for the unaged reference (Fig. 4.16). Thus, this experiment was able to recreate the colour of the naturally pre-aged reference.

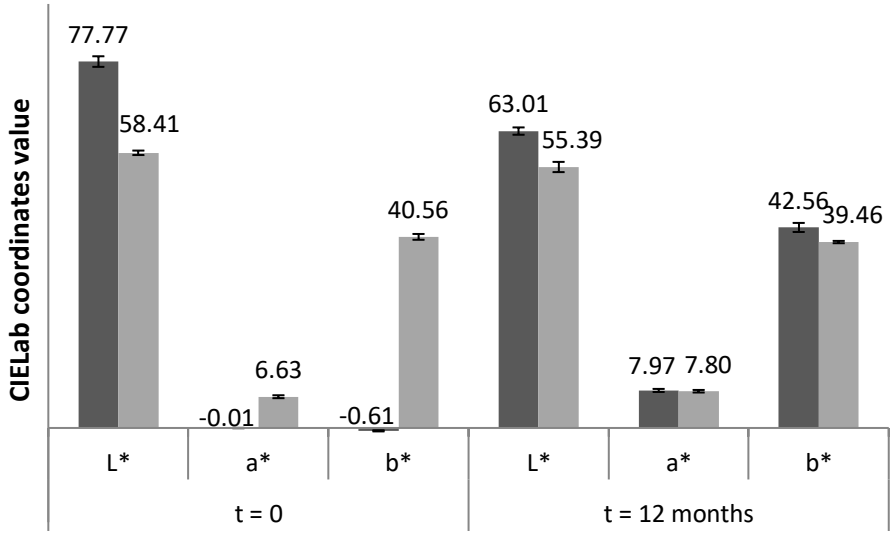


Figure 4.16 CIELab colour system coordinates for the unaged (dark grey) and naturally pre-aged (light grey) ether-based PUR foams before (t=0) and after (t=12 months) of natural ageing in the dark and in open-air.

Regarding the unaged reference during ageing, additional variations were detected for open-air at 1660, 1700 and 1712 cm^{-1}. Up to nine months of storage, the relative intensity of the shoulder at 1660 cm^{-1} increased in a large scale but after that, this tendency has been halted and a loss of intensity is observed, along with the loss of intensity at 1620 cm^{-1} (Figs. 4.11 and 4.13). This decrease could be related to possible chain scission mechanisms and/or to the formation of volatile compounds upon

ageing in open-air. In addition, the relative intensity of the bands at 1712 cm^{-1} and 1700 cm^{-1} also decreased (Figs. 4.11 and 4.13). Although the exclusive visual interpretation of the open-air plot could have suggested the existence of spectral variations at 1700 cm^{-1} already after one month, ANOVA with Post Hoc Tukey Kramer multiple comparison test has determined those variations as not significant (i.e. the values from each month are not significantly different) and therefore, they are all marked with the same letter (a) prior to 9 months. This proves the use of this statistical method as a valuable extra tool in the analysis of spectral data. Regarding the assignment of these variations, several authors have attributed them to hydrogen-bonding interactions on the PUR segregated structure (Romanova *et al*., 2002; Janik *et al*., 2003). The intensity variation at 1660 cm^{-1} may be related to the formation of new H-bonds on C=O groups from urea linkages and the successive loss of intensity at 1712 cm^{-1} to the loss of H-bonds on urethane linkages. In the enclosed storage at room T, although fewer variations were recorded, the band at 1700 cm^{-1} also showed a relative intensity increase (from 0.16±0.02 to 0.27±0.04). This spectral change may be assigned to a higher degree of short range hydrogen-bonding interactions on urethane linkages. Nevertheless, a considerable improvement on foam stability was observed just by placing the ether-based PUR foam samples in sealed bags (long-term storage in the dark, at room T) (Fig. 4.7).

Concerning the naturally pre-aged commercial reference (Fig. 4.17), although significant spectral changes were detected in the four storage conditions (at 1660 cm^{-1} and 1700 cm^{-1}), open-air storage clearly shows the highest changes, showing an increase of the relative intensities of these wavenumbers upon ageing. All other tested conditions proved to be more beneficial for the stability of the foams.

From the general assessment of these results, the high vulnerability of hydrogen-bonding interactions in ether-based PUR slabstock foams is emphasised. Not only significant changes were detected in samples which yellowed upon ageing (in open-air), as new H-bonds were formed on samples which did not suffer any clearly visible decay (enclosed systems). Furthermore, since the formation of hydrogen bonding plays a major role in the arrangement of PUR foams segregated structure (in HS and SS), the modification of these interactions results in drastic physical consequences. For example, in highly deteriorated cases (as shown in Chapter 3), these foams become viscous when compressed and completely lose their elasticity when handled. Since hydrogen bonding interactions are virtual crosslinks but 'act like "covalent crosslinks" at room temperature' (Thomas *et al*., 1994: 2156), their vulnerability may be one of the key aspects that dictate the short lifespan of PUR slabstock foams.

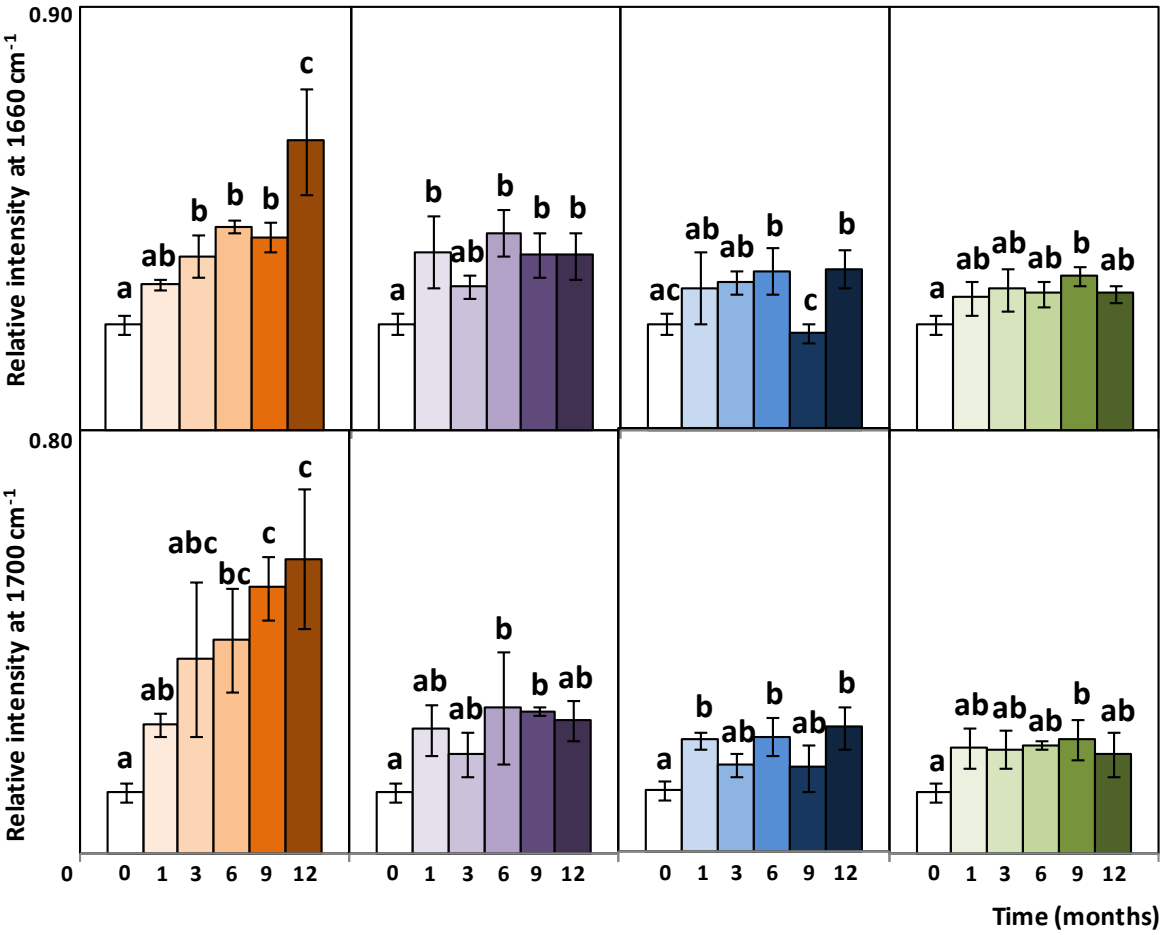


Figure 4.17 Raman intensities normalised for the C–H_2 bending (at 1455 cm^{-1}) of the naturally pre-aged ether-based PUR foam before (t=0, white bar) and after ageing (t=[1,12] months, colour bars) in different storage conditions: open-air storage (orange bars), enclosed storage (purple bars), cool-enclosed storage (blue bars) and anoxic storage (green bars). All values are means (bar) of triplicates ± SD (whiskers). Statistical significance for ANOVA and Tukey-Kramer multiple comparison tests was established at a *p*-value < 0.05. Values that are significantly different between times within the same storage are indicated by different lowercase letters.

In sum, open-air storage was definitely the most harmful condition for both unaged and naturally pre-aged ether-based PUR foams, anoxic and cool-enclosed storage showed promising results and simple enclosed systems proved to minimise colour changes (ΔE^*<2). Although the anoxic enclosure is the best storage condition for these foams, the improvement in stability compared to enclosed storage systems at room and low T (at 12°C) may not be significant enough to justify the required financial investment. Nevertheless, this dark storage ageing experiment is still ongoing and future results may help clarifying the pros and cons of each condition. Raman microscopy was able to translate clearly visible deterioration pathologies (such as yellowing) into new molecular spectral lines but, most important, to detect early molecular deterioration invisible for the human eye, such as, possible changes in PUR hydrogen-bonding interactions.

The following section discusses the same ageing experiment but for ester-based PUR foams.

4.2.3. Ester-based PUR slabstock foams

Similarly to the previous section (4.2.2), since both ester-based references showed comparable results upon ageing, only the data concerning the unaged reference is discussed in detail.

4.2.3.1 Ester-based PUR foam references characterisation

The characterisation of the unaged ester-based reference by OM and IR spectroscopy was already discussed in Chapter 3 (section 3.4.1.1). For that reason, only main differences regarding the naturally pre-aged reference (produced in c. 2006 and showing a fair condition) are discussed. From optical microscopy, the main difference between the two references is the intensity of fluorescence (Fig. 4.18 compared to Fig. 3.23). As expected, although both references show fluorescence under blue-violet and ultraviolet wavelengths, the unaged reference shows a weaker fluorescence intensity.

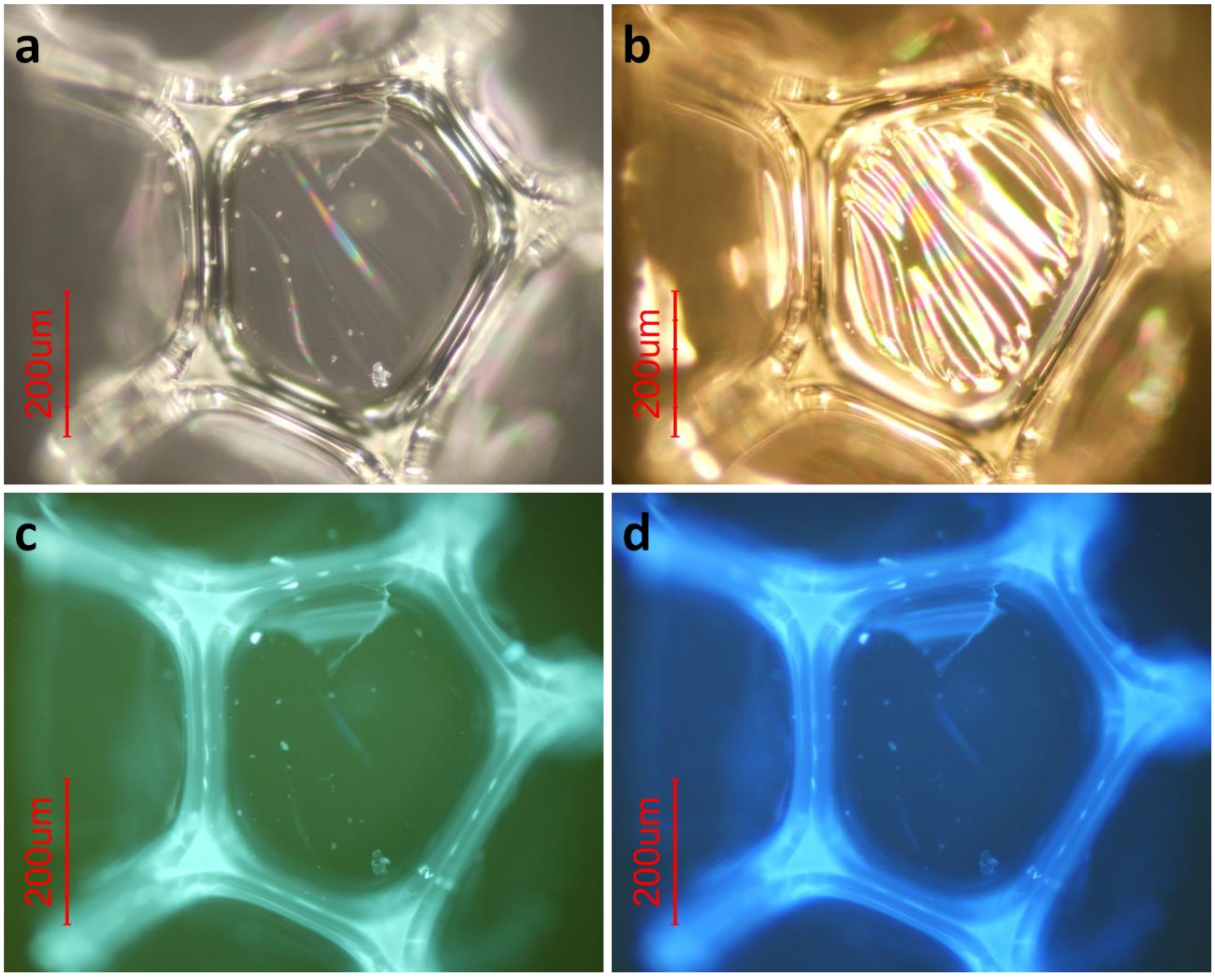


Figure 4.18 Microscopy images of the naturally pre-aged ester-based PUR foam under cross-polarised light (a), darkfield (b), blue-violet light (c) and ultraviolet light (d).

From IR spectroscopy, both references show the characteristic bands of ester-based PUR slabstock foams (Fig. 4.19) (Pellizzi *et al*., 2014, 2016; Lattuati-Derieux *et al*., 2011; Lovett & Eastop, 2004). On the other hand, the spectral differences detected between the two references result from their different condition (good - unaged reference; and fair - naturally pre-aged reference) (Fig. 4.19). From the unaged to the naturally pre-aged foam, a decrease of C–H, C=O and C–O–C stretching bands relative intensities is observed between 2900–2800, 1750–1700 and 1200–1000 cm^{-1}, respectively (Fig. 4.19). As supported by literature, these changes are assigned to the deterioration of the ester-based SS domain (Pellizzi *et al*., 2014), which indicates the higher degradation of the naturally pre-aged reference. Besides, significant shifts in the N–H (Fig. 4.19) and C=O (Fig. 4.19, inset) stretching regions are observed. Along with the C=O shift from 1643 cm^{-1} (strong H-bonded urea) to 1655 cm^{-1}, the N–H band shifts from 3320 cm^{-1} to higher frequencies, 3344 cm^{-1}. Consequently, the naturally pre-aged reference may have suffered a disarrangement (disordering) of the HS domain, as well as the scission of some ester groups from the SS domain.

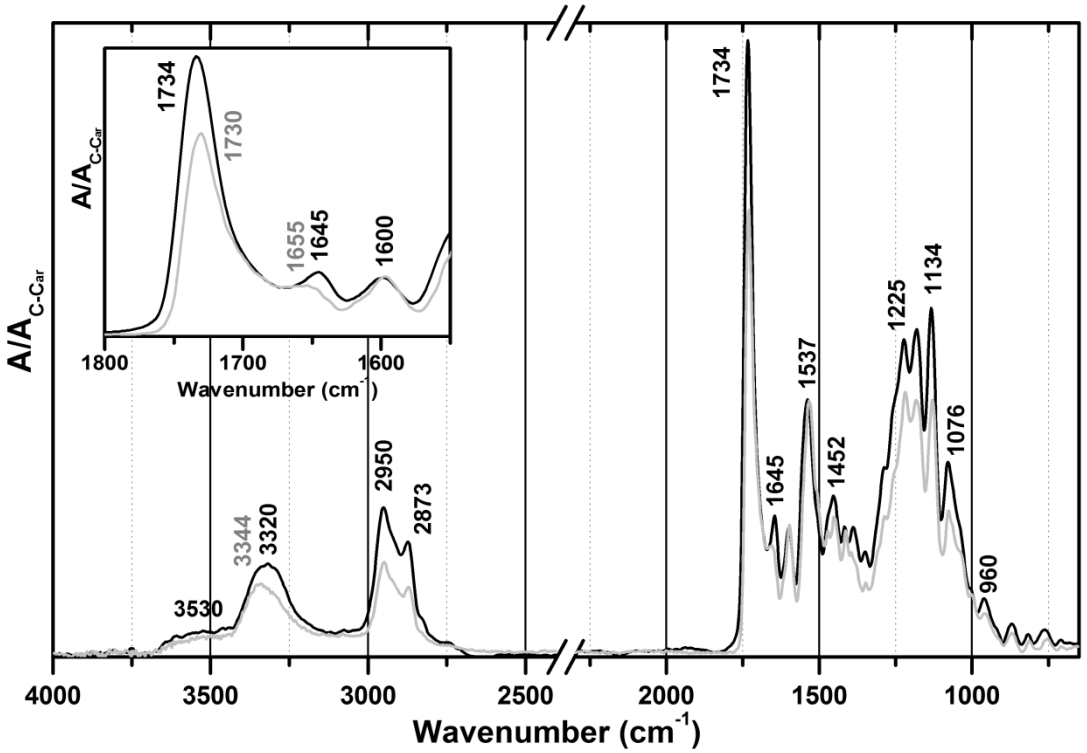


Figure 4.19 Infrared spectra of the unaged (black) and naturally pre-aged (grey) ester-based PUR foams. Inset: Detail of the carbonyl region from 1800 to 1550 cm^{-1}.

From Raman microscopy, complementary information was obtained and once more, earlier Raman studies on model TPUs were used as references for the assignment of the bands of the ester-based PUR references (Miller *et al*., 1990; Hu *et al*., 1992; Romanova *et al*., 2002; Janik et al., 2003; Parnell *et*

al., 2003; Bruckmoser & Resch, 2014 and citations therein). Since comparable bands are recorded between ether- and ester-based PUR references (see section 4.2.2.1), only main differences are highlighted, which, in short, result from the presence of a different SS type (ester-based and not ether-based) (Figs. 4.20 and 4.21). As characteristic of ester-based PUR, instead of the small relative intensity band at 1712 cm^{-1} (C=O stretching), the ester-based references show a stronger band at 1728 cm^{-1} (C=O stretching). Moreover, only two overlapping bands between 1000–1200 cm^{-1} are recorded (maxima at 1054 and 1080 cm^{-1}), in contrast with the four overlapping bands of the ether-based PUR foams spectra (maxima at 1057, 1084, 1133 and 1162 cm^{-1}). In the ester-based PUR Raman spectrum, the band at 1133 cm^{-1} looses intensity and the band at 1162 cm^{-1} disappears. Regarding the region between 2700–3500 cm^{-1}, the absence of the band at 2972 cm^{-1} is also observed, as consequence of the absence of C–H_3 groups in ester-based SS. Since these differences indicate the presence of a different SS type in the PUR molecular structure, the combined presence of a complex band with maxima at 1054 and 1080 cm^{-1} (C–O–C stretching), a band at 1728 cm^{-1} (C=O stretching) and the absence of a band at 2972 cm^{-1} may be used as Raman markers for the distinction between ether- and ester-based PUR foams.

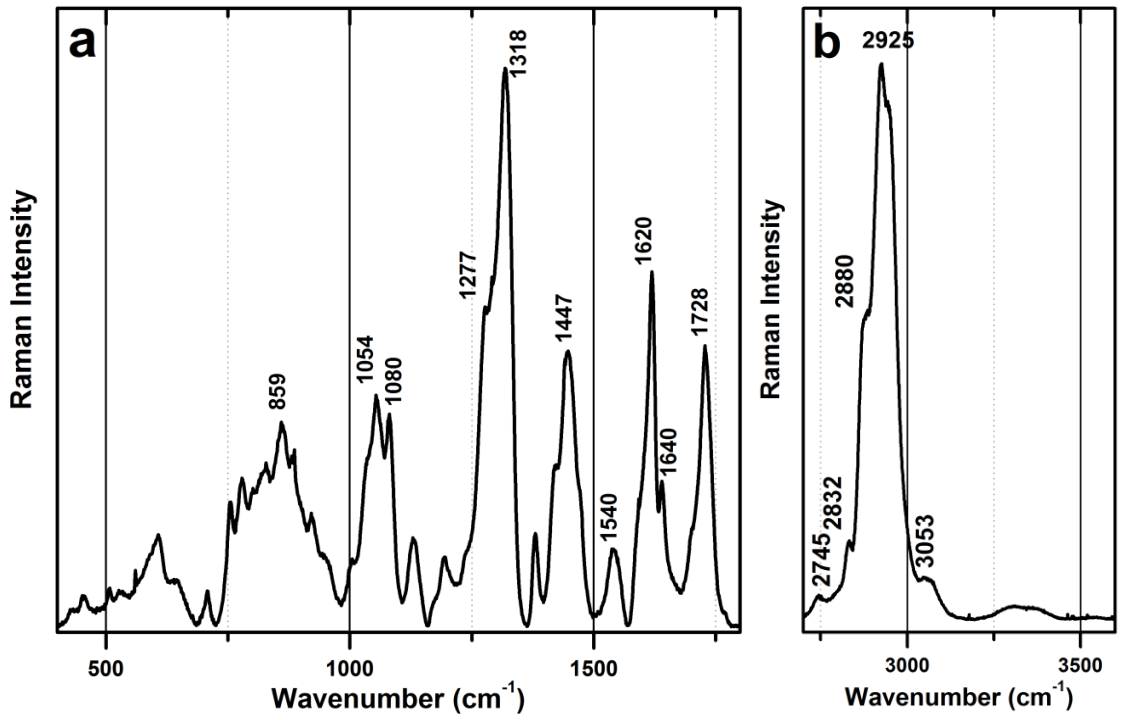


Figure 4.20 Raman spectra of the unaged ester-based PUR foam from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

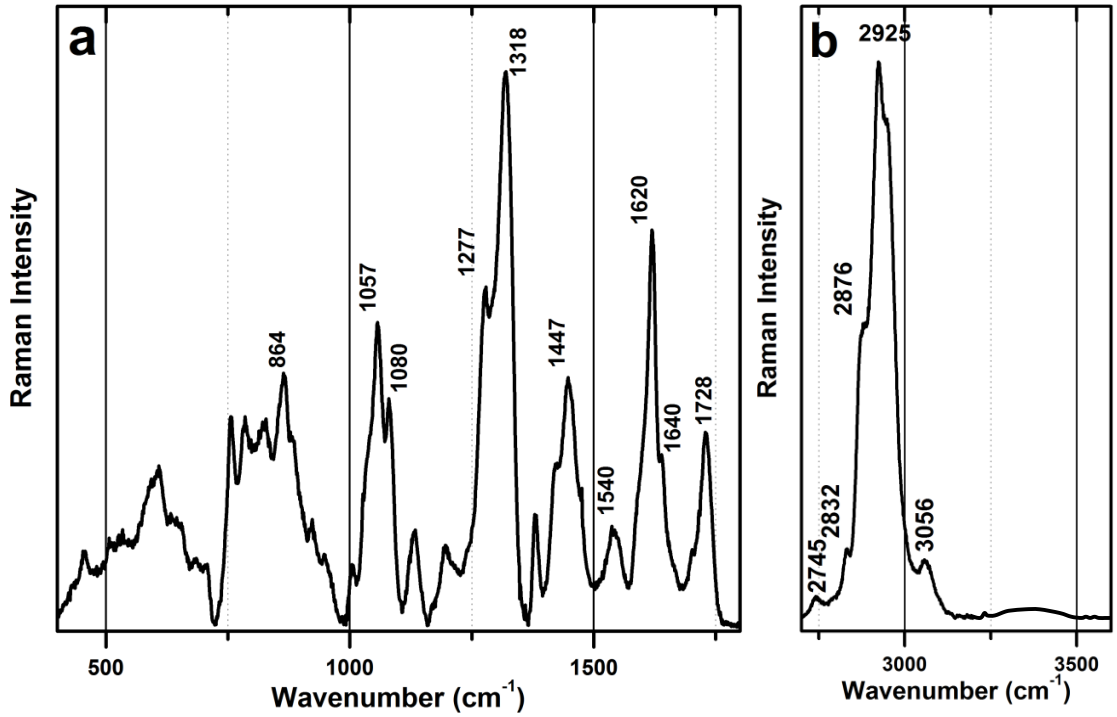


Figure 4.21 Raman spectra of the naturally pre-aged ester-based PUR foam from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

When the unaged and the naturally pre-aged references are compared, the C=O band from the unaged reference is more intense (Fig. 4.22), which corroborates the results from IR spectroscopy and the attribution of this change to different condition grades.

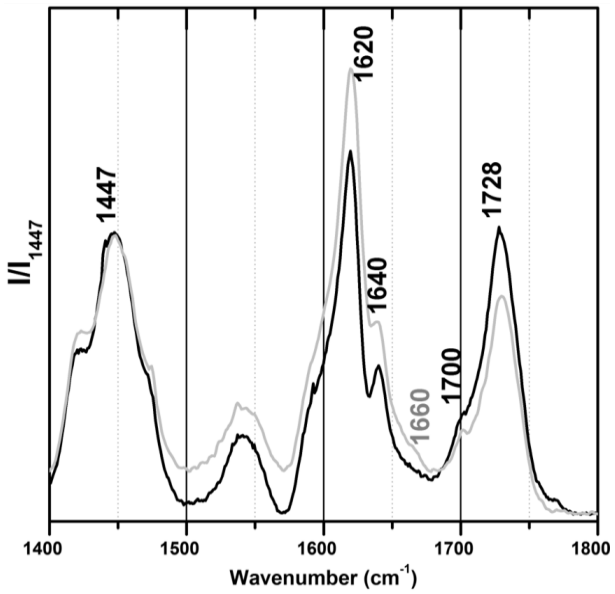


Figure 4.22 Raman spectra of the unaged (black) and naturally pre-aged (grey) ester-based PUR foam from 1400 to 1800 cm^{-1}.

As previously explained (section 4.2.2.1), hydrogen-bonding interactions can be characterised from the careful analysis of the C=O stretching region in Raman spectra. According to Weakley *et al*., the carbonyl stretching shoulder observed at 1700 cm^{-1} and the band at 1728 cm^{-1} may be assigned to ordered HS domains and free C=O stretching frequencies from both the hard- and soft-segments, respectively (Weakley *et al*., 2012 and citations therein). Since the naturally pre-aged reference shows the decrease of both these bands and the increase of a band at 1660 cm^{-1} (previously assigned to H-bonded C=O groups from urea linkages), in sum, these changes may reflect the degradation of ester groups but also the formation of new H-bonds. In addition to what was explained before, this may also indicate the more degraded condition of the naturally pre-aged reference, but further research on ester-based PUR foams by Raman spectroscopy should be carried out in order to confirm these hypotheses.

4.2.3.2 Assessment of the dark ageing experiment

In comparison with the previous case (ether-based references), these foams showed a slower rate of deterioration (under the same ageing conditions). Consequently, the visual alterations were less intense (e.g. yellowing) and the detected spectral changes were less conclusive about which storage provides the best condition for their preservation. However, this situation was not unexpected since the ageing was carried out in the dark, at room or low T and at 45–55% RH, and the deterioration dependence on oxygen of ester-based PUR foams is much lower than ether-based PUR foams (Rychlý *et al*., 2011). As some contributions to the long-term storage of these foams are launched, the main results are discussed in the following paragraphs.

From the gravimetry assessment upon ageing, once more, no relevant results (and no tendency) were obtained (weight variations below 0.7%) (see Appendixes V.3 and V.4).
Under the stereomicroscope, the most noticeable difference was yellowing, which was exclusively detected on the samples kept in open-air (Fig. 4.23). For the unaged reference, while open-air storage resulted in total colour variations close to twenty ($\Delta E^* \approx 19$) after 12 months of ageing in the dark, the enclosed systems (room T, low T and anoxic) prevented discoloration during the entire ageing experiment ($\Delta E^* < 2$).

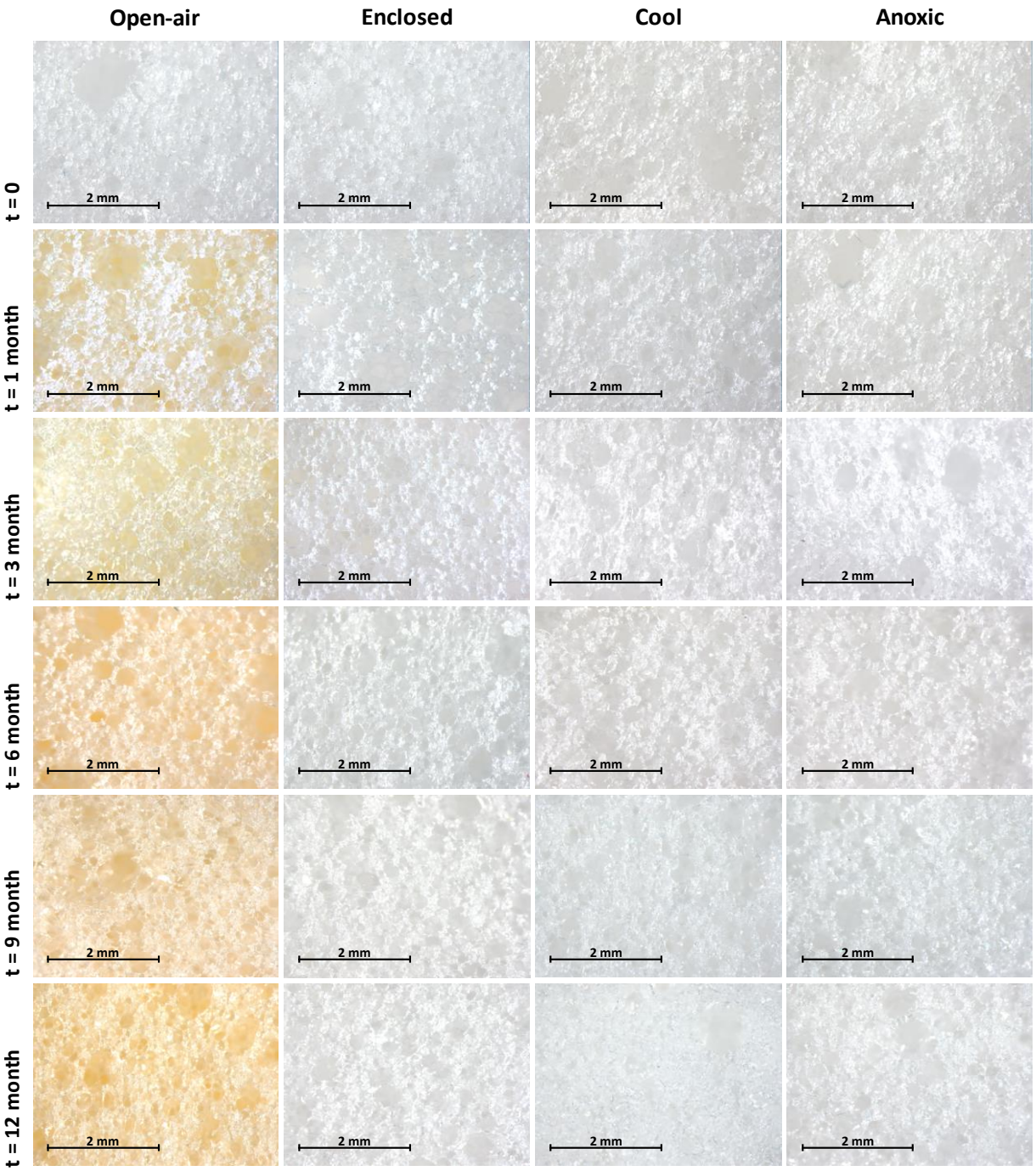


Figure 4.23 Stereomicroscopy images of the unaged ester-based PUR before (t=0) and after ageing (t=[1,12] months) in the dark in different storage conditions. Each image corresponds to a different foam sample.

Concerning the naturally pre-aged reference, comparable results were obtained. The samples exposed in open-air suffered total colour variations close to seven ($\Delta E^* \approx 6.8$) after twelve months of ageing, whereas values below one were obtained for the samples kept in enclosed systems. Once more, this highlights oxygen as one of the main potential causes for PUR foam yellowing. For that reason, the urgency of studies discussing the exclusive role of light and oxygen in the discolouration of PUR foams

is stressed, especially because important contributions might be launched for the definition of optimum display conditions for PUR-based objects in museum collections.

Colourimetry was also able to detect different rates of yellowing (through b* coordinate increase) between ether- and ester-based PUR foams under the same ageing conditions. Even though both references were made with aromatic diisocyanates (TDI), showed a white colour at the beginning of the experiment and the presence of aromatic structures has been mentioned as the main cause of PUR yellowing, the yellowing increase in the unaged ester-based PUR was much lower than in the unaged ether-based PUR ($\Delta b^*_{\text{ester-based PUR}} \approx 18$, while $\Delta b^*_{\text{ether-based PUR}} \approx 43$ — both in open-air)[105] (Fig. 4.24).

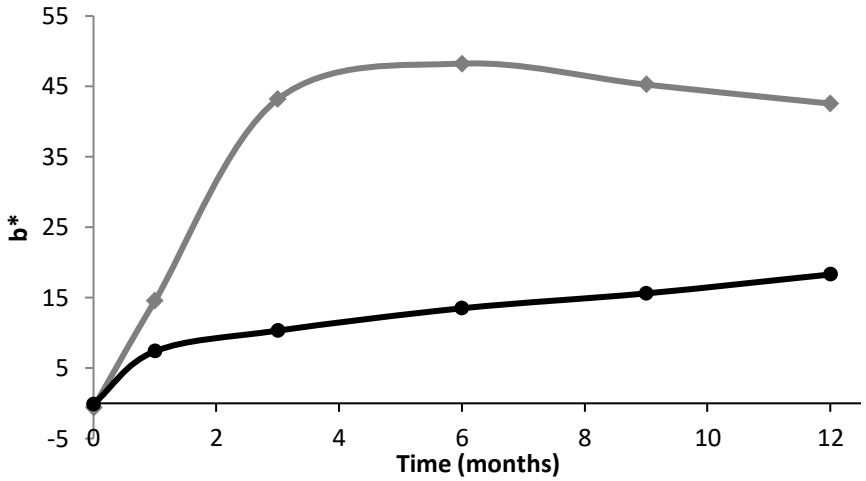


Figure 4.24 Progression of b* coordinate upon the ageing (open-air) of ether- (grey) and ester-based (black) unaged PUR foam references in the dark.

This highlights the great influence of the SS type in the yellowing rate of PUR foams in dark ageing conditions. A possible justification could be the already recognised lower oxidation resistance of ether-based PURs, when compared to ester-based PURs. According to Dieter Dieterich, oxidation of polyether polyols can occur in the absence of light (Dieterich, 1992). Accordingly, Szycher mentions that if ester is the weakest link in hydrolysis, ether is the weakest link in thermo-oxidation (thermo-oxidation stability order: ester > urea > urethane > ether), proceeding via a free radical mechanism (Szycher, 2013: 23). From this, peroxide radicals, hydroperoxides, oxide radicals and hydroxyl free radicals can be formed, possibly leading to foam yellowing (formation of quinoid-type structures) through subsequent reactions in the HS domain. Furthermore, by comparing different polyether polyols (PTMEG, PEG and PPG), Szycher mentions PPG as the most prone (and mostly used in PUR flexible foams) to thermal-oxidation (Szycher, 2013).

[105] This was also observed in the naturally-aged references.

From conventional light microscopy, yellowing and/or the formation of defects in the foam cell buns upon ageing were not detected, even in the samples kept in open-air (Fig. 4.25.a,b).

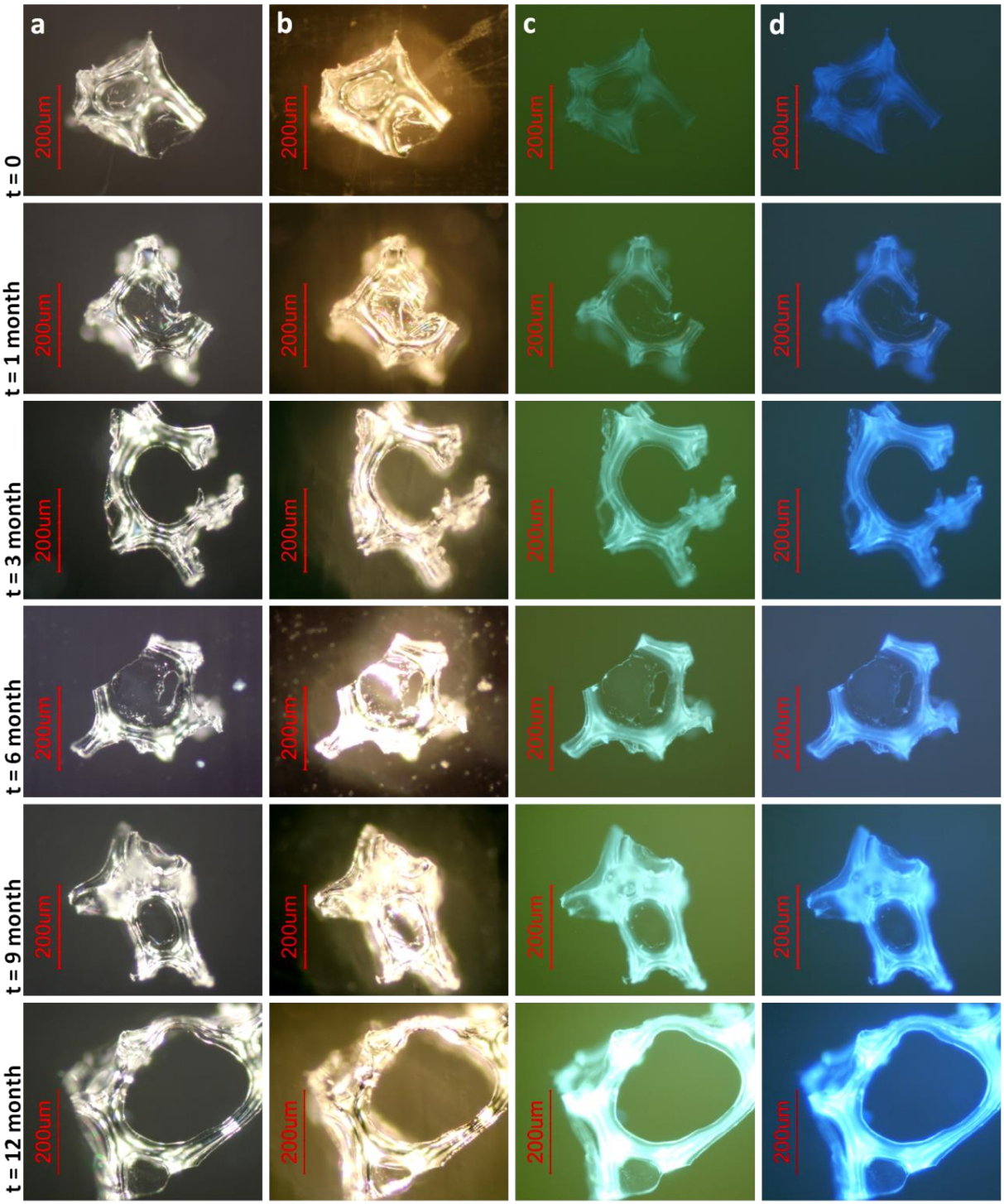


Figure 4.25 Microscopy images of the unaged ester-based PUR foam before (t=0) and after ageing (t=[1,12] months) in open-air: cross polarised light (column a), darkfield (column b), blue-violet light (column c) and ultraviolet light (column d).

On the other hand, the analysis of the PUR cell buns fluorescence under blue-violet and ultraviolet lights enabled the detection of different fluorescence intensities in these samples (Fig. 4.25c,d). There is an increase in the fluorescence intensity of the foams upon ageing in open-air conditions, which, once more, highlights this contrast mode as an important tool for the detection of the increase in the formation of chromophores in polymer networks.

In contrast to conventional light microscopy, confocal microscopy was able to reveal the formation of damages (micro-holes) at the surface of the cell struts in both references in open-air (Figs. 4.26 and 4.27).

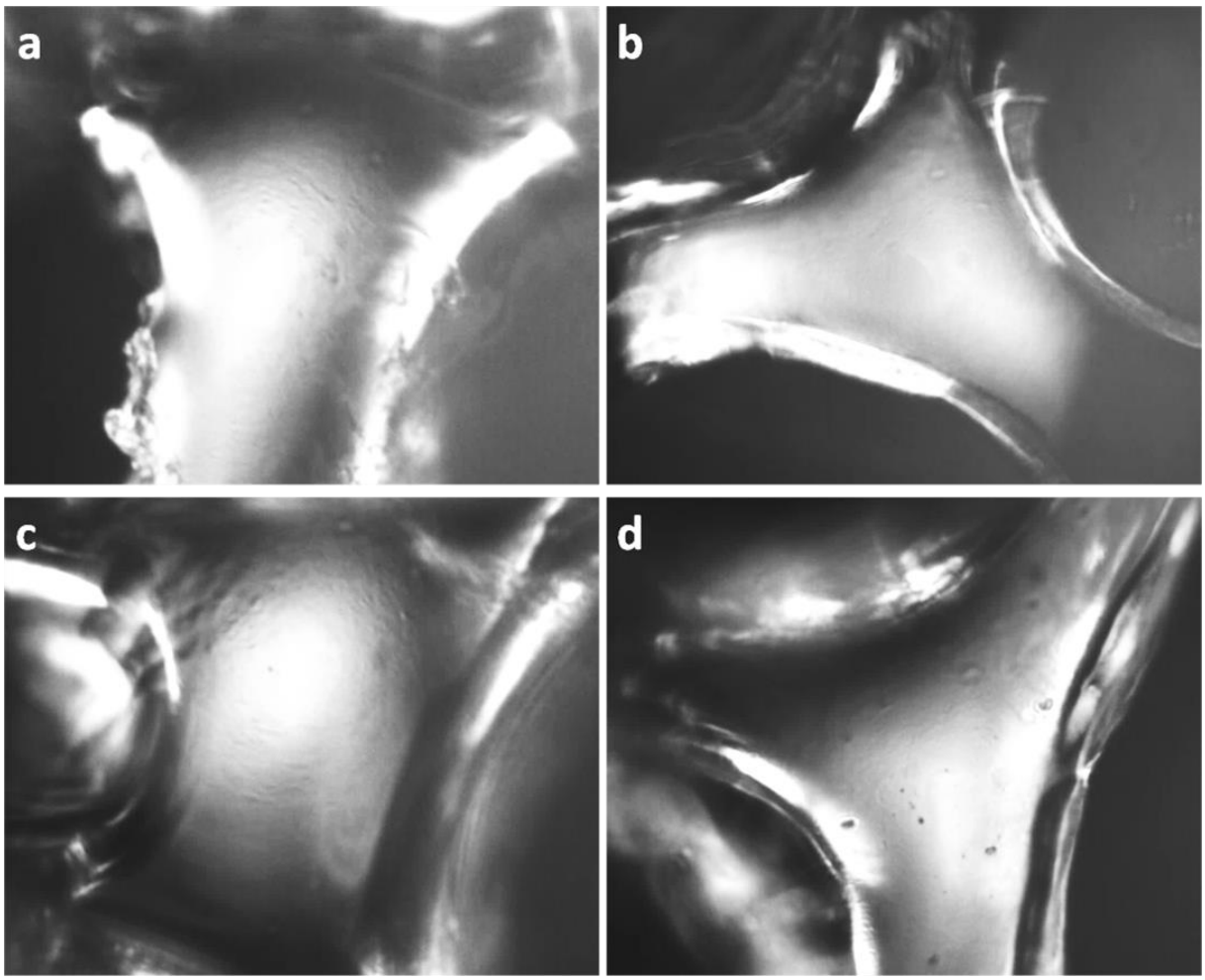


Figure 4.26 Confocal microscopy images (500x) of the unaged ester-based PUR foam cell struts after 12 months in dark ageing at different storage conditions: anoxic (a), cool-enclosed (b), enclosed (c) and open-air (d).

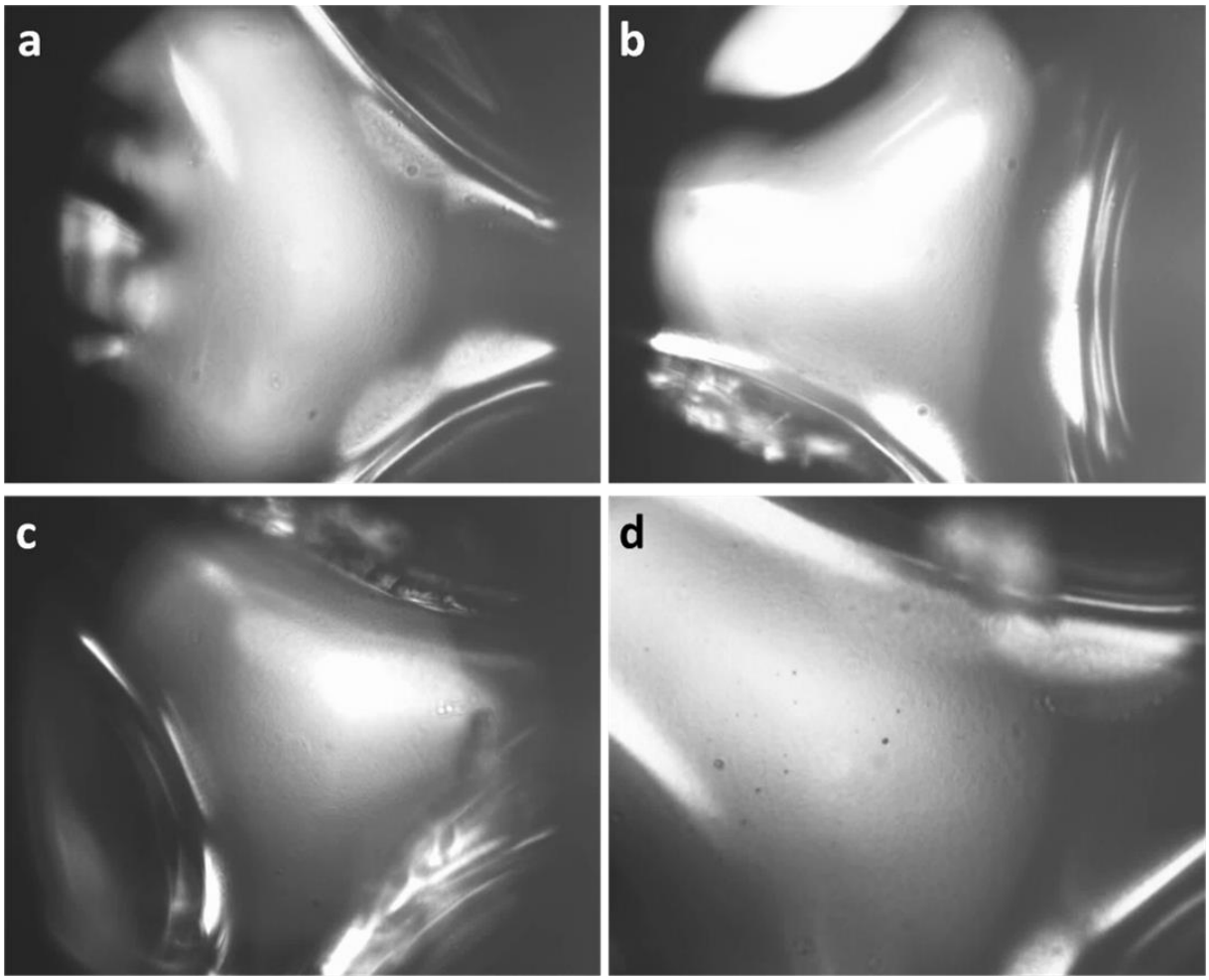


Figure 4.27 Confocal microscopy images (500x) of the naturally pre-aged ester-based PUR foam cell struts after 12 months in dark ageing at different storage conditions: anoxic (a), cool-enclosed (b), enclosed (c) and open-air (d).

From IR spectroscopy, it was not possible to distinguish which is the best storage condition (see Appendixes V.3 and V.4).

From Raman spectroscopy, although more conclusive results were obtained, the data did not show a clearly distinguishable degradation course between the four storage conditions as found for the ether-based PUR references. Within the selected region for this assessment (1600–1800 cm^{-1}, C=C and C=O stretching), only the band shoulders at 1660 and 1700 cm^{-1} showed the most conclusive results[106] (Figs. 4.28 and 4.29). However, these bands relative intensities do not show a degradation tendency, i.e. there is no continuum increase (or decrease) in their relative intensities (in relation to t=0) upon ageing. Nevertheless, in general, open-air storage showed the highest variations upon ageing (Figs.

[106] Similarly to section 4.2.2, spectral changes are expressed as mean and standard deviation values. For each wavenumber, the three independent measurements were statistically evaluated by ANOVA test (analysis of variance) in order to identify significant variations upon exposure.

4.28 and 4.29), whereas anoxic stood out as a promising preventive measure (no significant spectral differences were detected, *p*-value above 0.05). Cool-enclosed storage showed positive results and once more, simple enclosed systems proved to minimise colour changes (ΔE*<2).

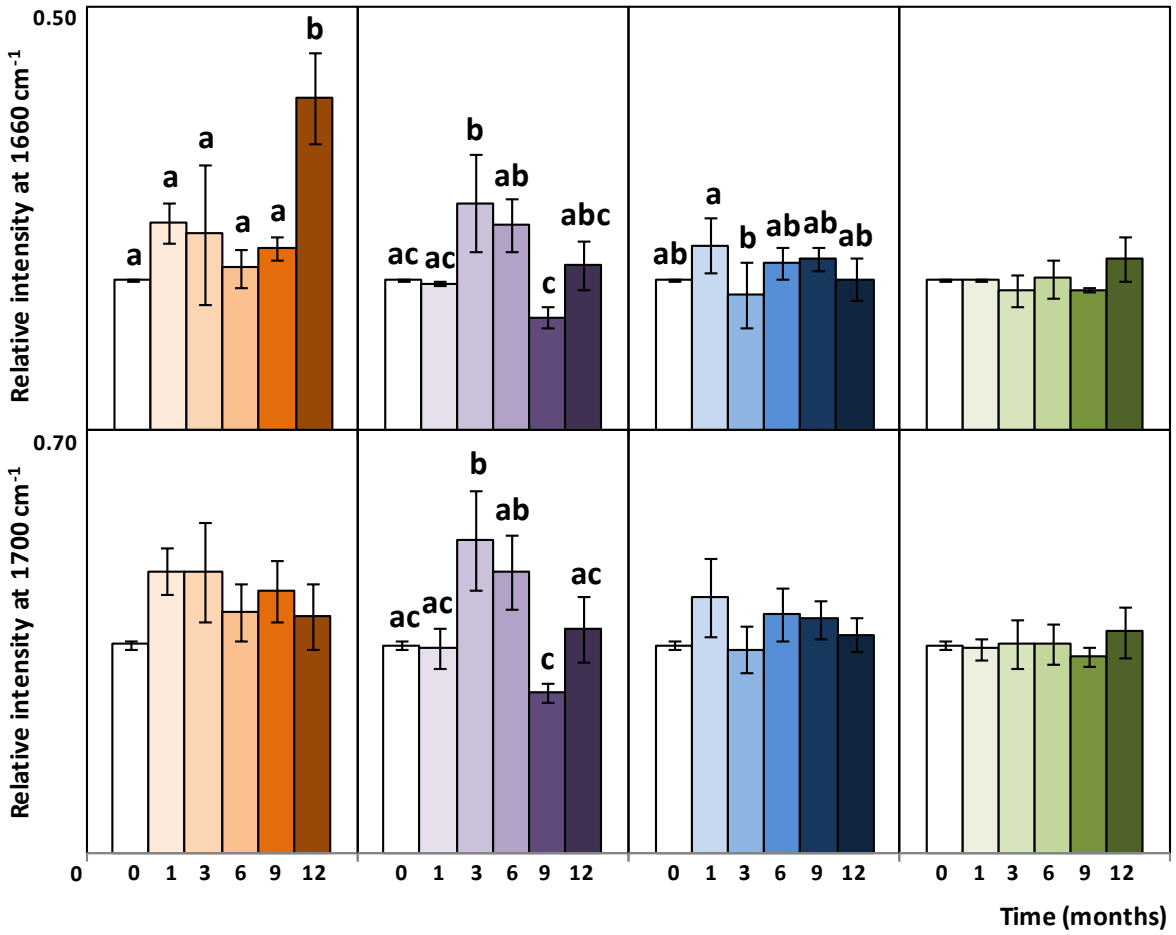


Figure 4.28 Raman intensities normalised for the C–H_2 bending (at 1447 cm^{-1}) of the unaged ester-based PUR foam before (t=0, white bar) and after ageing (t=[1,12] months, colour bars) in different storage conditions: open-air storage (orange bars), enclosed storage (purple bars), cool-enclosed storage (blue bars) and anoxic storage (green bars). All values are means (bar) of triplicates ± SD (whiskers). Statistical significance for ANOVA and Tukey-Kramer multiple comparison tests was established at a *p*-value < 0.05. Values that are significantly different between times within the same storage are indicated by different lowercase letters.

As 1700 cm^{-1} and 1660 cm^{-1} C=O stretching bands have been assigned to hydrogen-bonding interactions (as explained before), once more, these secondary bonds are proved to be highly unstable even in standard storage conditions such as in the dark, room T and at 45–55% RH.

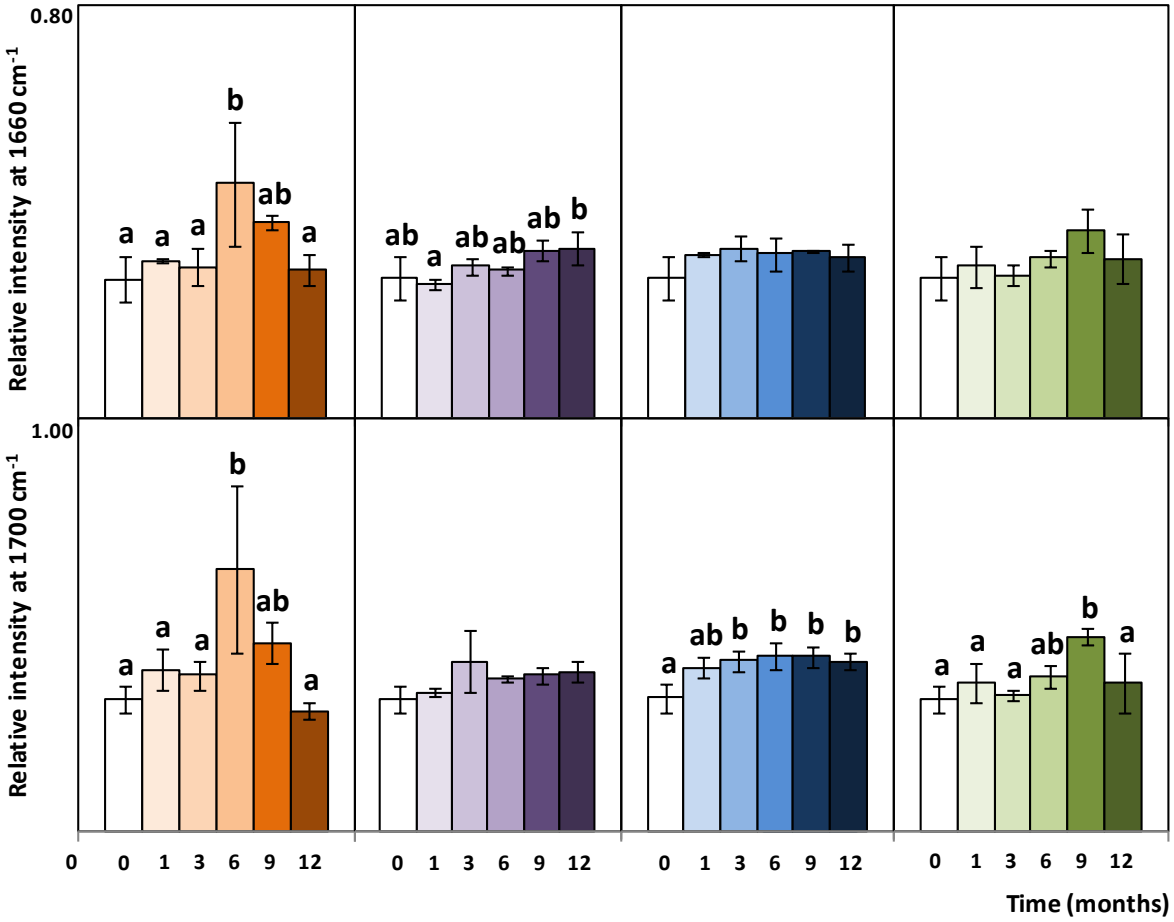


Figure 4.29 Raman intensities normalised for the C–H_2 bending (at 1447 cm^{-1}) of the naturally pre-aged ester-based PUR foam before (t=0, white bar) and after ageing (t=[1,12] months, colour bars) in different storage conditions: open-air storage (orange bars), enclosed storage (purple bars), cool-enclosed storage (blue bars) and anoxic storage (green bars). All values are means (bar) of triplicates ± SD (whiskers). Statistical significance for ANOVA and Tukey-Kramer multiple comparison tests was established at a *p*-value < 0.05. Values that are significantly different between times within the same storage are indicated by different lowercase letters.

4.2.4. Ester-based TPU films

Similarly to the previous sections (4.2.2 and 4.2.3), two references were included in this ageing experiment, unaged and naturally pre-aged. The TPU film already discussed in Chapter 3 was selected as the unaged reference, whereas a TPU-based leather from a bag with c. 10 years of use was chosen as the naturally pre-aged reference. However, due to the texture, dark blue colour and dirt/residues deposited at the surface of the dark blue leather, the results from its ageing assessment were

inconclusive[107] and consequently, disregarded for this discussion. For that reason, only the data concerning the unaged TPU film is discussed.

4.2.4.1 Ester-based TPU film reference characterisation

The information concerning the visual (by OM) and molecular (by IR spectroscopy) characterisation of the unaged TPU film was already discussed in Chapter 3.
From stereomicroscopy, the transparency and the clean surface of the unaged film is clearly visible (Fig. 4.30). These films were analysed deposited onto glass slides and the images from the stereomicroscope were acquired with the glass/film sample placed on white printing paper.

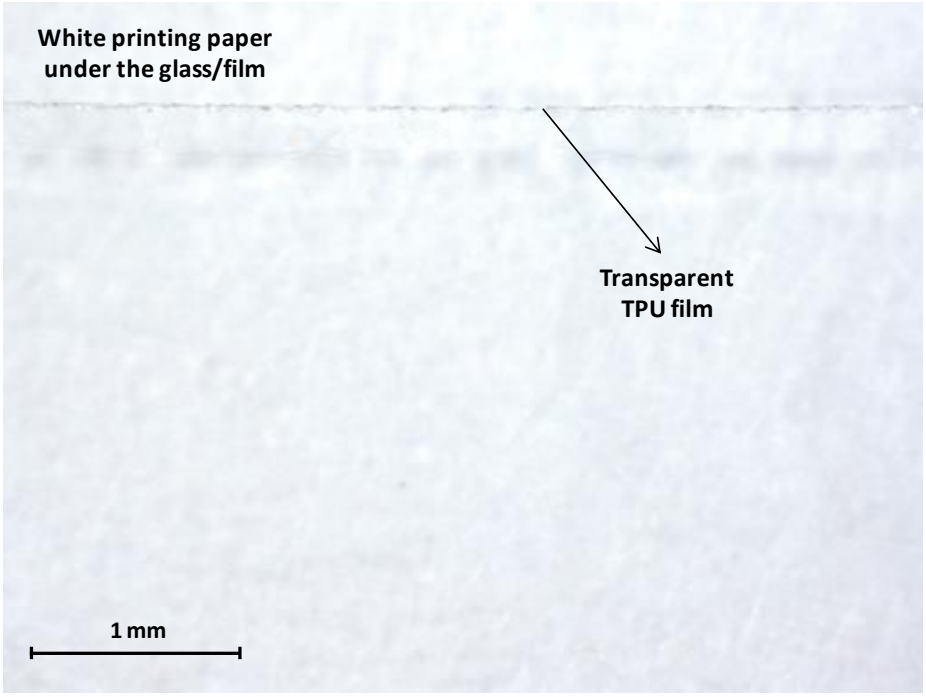


Figure 4.30 Stereomicroscopy image of the surface of the unaged ester-based TPU film.

From Raman spectroscopy (Fig. 4.31), characteristic bands as found on ester-based TPUs are detected (Parnell *et al*., 2003; Bruckmoser & Resch, 2014 and citation therein). The ester-based SS of the TPU in study is detected at c. 1730 cm^{-1} (C=O stretching), at c. 1438 cm^{-1} ($C–H_2$ bending), and at c. 2880 and 2925 cm^{-1} ($C–H_2$ stretching). The aromatic rings from the HS can be identified by the bands at c. 1184 cm^{-1} (=C–H in plane deformation), at c. 1616 cm^{-1} (–C=C stretching) and at c. 3065 cm^{-1} (=C–H

[107] Furthermore, Raman spectroscopy was not possible to use due to the burning caused by the Raman laser power on the dark surface of the artificial leather.

stretching), whereas the urethane groups are detected by the bands at c. 1250 cm^{-1} (coupled C–N stretching and N–H bending), at c. 1535 cm^{-1} (combined C–N stretching and N–H bending) and at c. 1700 cm^{-1} (C=O stretching). The bands detected between 1000–1155 cm^{-1} might be attributed to C–O groups, also from the urethane linkage.

Regarding the H-bonds, the carbonyl stretching band at c. 1700 cm^{-1} might be assigned to H-bonded C=O groups from urethane linkages, i.e., to ordered HS domains.

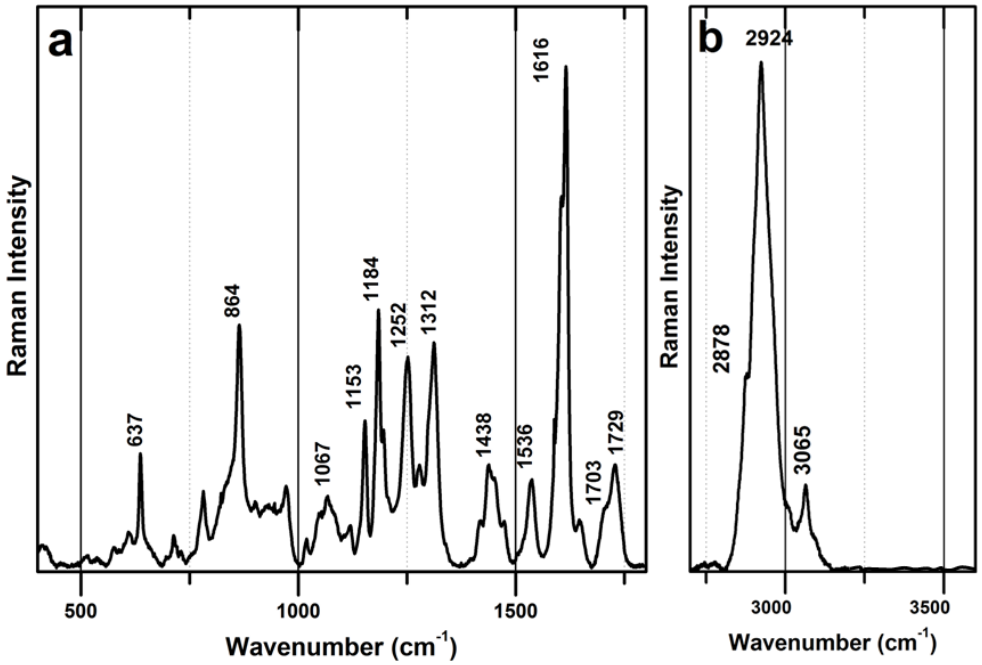


Figure 4.31 Raman spectra of the unaged ester-based TPU film from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

4.2.4.2 Assessment of the dark ageing experiment

While PUR foams are known for their high susceptibility to yellowing and crumbling (or to a complete loss of physical properties) within a few decades, and many studies have been focused on their consolidation (van Oosten, 2011), TPU films show (in general) longer lifespan than foams, and are not commonly addressed in conservation studies. Accordingly, in comparison with the PUR foams previously discussed (sections 4.2.1 and 4.2.2), the TPU samples in study showed a much slower rate of degradation and most of the assessing techniques indicate their stability upon this ageing. There were no noticeable differences in total colour variations (ΔE^*<1.3) for all storage conditions, weigh measurements showed no relevant variations (below 0.5%) (see Appendix V.5.1), stereomicroscopy and OM (see Appendixes V.5.2 and V.5.3) did not show any physical changes or fluorescence intensity

increase, and finally, both IR and Raman spectroscopies did not show spectral differences between unaged and aged samples, even after 12 months of exposure (see Appendixes V.5.4 and V.5.5). The only exceptions were the contact angle and the hardness (Shore A) measurements, which showed significant changes during ageing (*p*-value below 0.05).

The measurement of contact angles is commonly used to study the hydrophobic/hydrophilic properties of polymeric films (Hyder *et al.*, 2006; Rosa & Pinho, 1997; Yuan & Lee, 2013), and the effect of conservation procedures such as cleaning methods for plastics (Balcar *et al.*, 2012). For that reason, this technique was selected. Hydrophobic surfaces have high contact angles (>90°), whereas hydrophilic surfaces show low contact angles (<90°) (Rosa & Pinho, 1997; Yuan & Lee, 2013). At t=0, the TPU film in study showed a contact angle of c. 67°, indicative of a hydrophilic film. During the dark ageing experiment, although significant differences were detected in all storage conditions, none surpassed the 90° barrier (Fig. 4.32). Thus, the TPU films remained hydrophilic during the entire ageing experiment, independently of their storage condition. Anoxic storage showed the lowest variation (from 64° to 74°), whereas open-air showed the highest deviation from t=0 (from 67° to 86°).

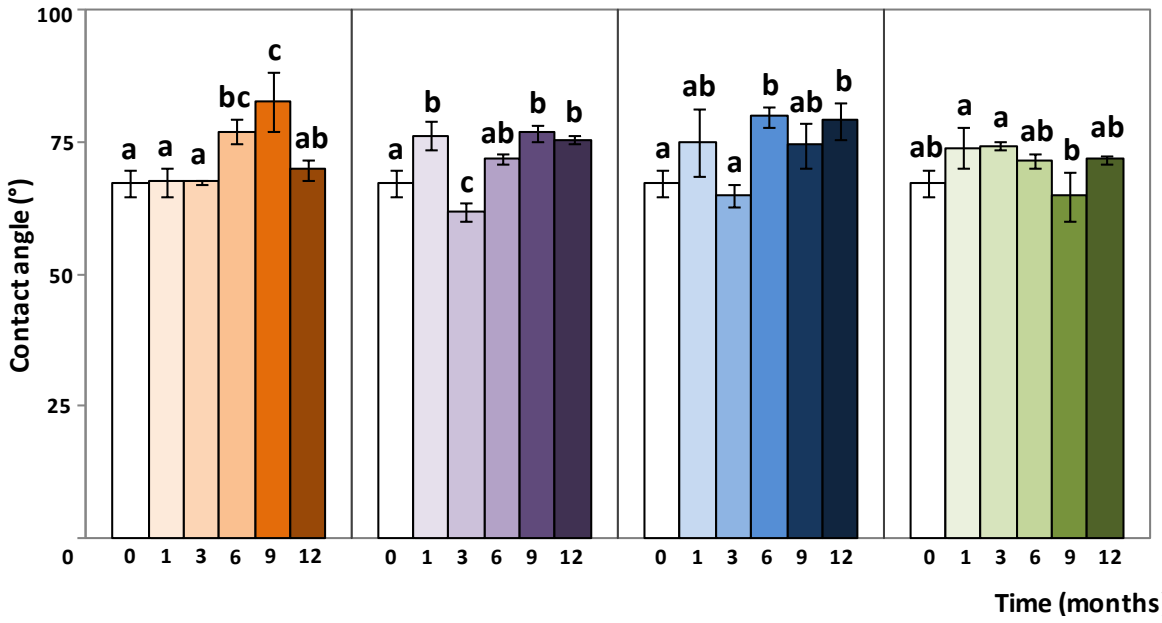


Figure 4.32 Contact angle (°) of the unaged ester-based TPU film before (t=0, white bar) and after ageing (t=[1,12] months, colour bars) in different storage conditions: open-air storage (orange bars), enclosed storage (purple bars), cool-enclosed storage (blue bars) and anoxic storage (green bars). All values are means (bar) of triplicates ± SD (whiskers). Statistical significance for ANOVA and Tukey-Kramer multiple comparison tests was established at a *p*-value < 0.05. Values that are significantly different between times within the same storage are indicated by different lowercase letters.

From the hardness (Shore A) measurements, additional results were obtained (Fig. 4.33). While open-air and enclosed conditions showed significant differences upon ageing (p-value < 0.05), cool-enclosed and anoxic storage did not affect this property. Moreover, an increasing trend in the hardness of the TPU films exposed to open-air and enclosed conditions was registered. This may indicate these conditions as promoters of film hardening and suggests an increase in the polymers' crystallinity and/or the occurrence of crosslinking reactions with ageing (Gulmine *et al*., 2003).

Accordingly, by comparing hardness and contact angle measurements, open-air storage can be considered the less benefic condition for the preservation of ester-based TPU films. It is also possible to conclude that ester-based TPU films show a far superior stability than PUR foams, even in open-air. For that reason, although open-air showed the most harmful results, this condition might be considered (if necessary) as a temporary storage for ester-based TPU films.

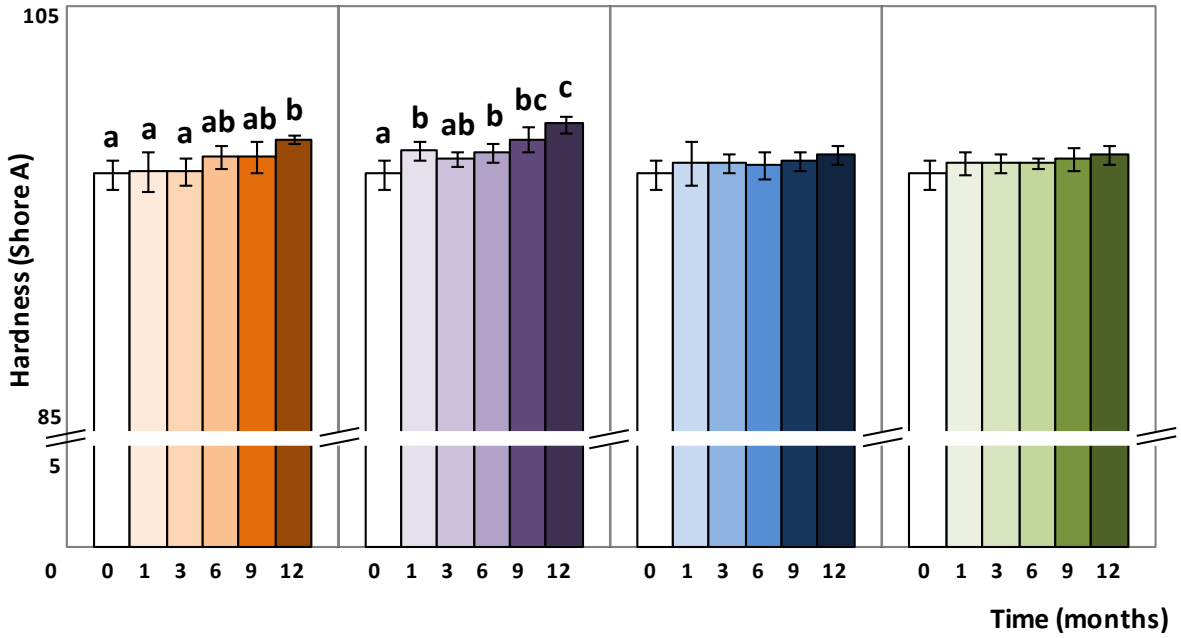


Figure 4.33 Hardness (Shore A) of the unaged ester-based TPU film before (t=0, white bar) and after ageing (t=[1,12] months, colour bars) in different storage conditions: open-air storage (orange bars), enclosed storage (purple bars), cool-enclosed storage (blue bars) and anoxic storage (green bars). All values are means (bar) of triplicates ± SD (whiskers). Statistical significance for ANOVA and Tukey-Kramer multiple comparison tests was established at a p-value < 0.05. Values that are significantly different between times within the same storage are indicated by different lowercase letters.

As MUDE collection holds some PUR-based objects already showing degradation, and some are considered total losses, the following section discusses conservation strategies that might be applied to those objects in order to allow their future communication to the public.

4.3 Ethical and theoretical dilemmas involved in the decision-making process for the conservation of PUR in fashion and product design – a brief discussion

As explained before, the MUDE collection includes iconic furniture pieces, utilitarian objects, garments and accessories, all part of the design and fashion history of the 20th century. Given the collection's significance, the establishment of a conservation plan is crucial, especially when some important historical icons are at risk of loss, as some showing PUR and discussed in Chapter 3. Similarly to MUDE, more and more, modern and contemporary museum collections hold objects based on PUR, especially because this polymer has been highly appreciated by artists, designers and industrials since the late 1960s (van Oosten, 2011). On the other hand, when this polymer enters into museum collections, it is known by its ephemeral nature (Lattuati-Derieux *et al*., 2011). To the current knowledge, after degradation starts, damage is irreversible and only consolidation and/or stabilisation may be considered to preserve the original materiality of the object; although, in some cases, even these hypotheses are not realistic. In addition to these drawbacks, even in controlled environmental conditions PUR continues to degrade and in a near future, the exhibition of these objects is at risk. From this background, the conservation challenges raised by the presence of polyurethane in cultural assets are highly demanding and unavoidable – requiring the careful assessment of the values embodied in each object, the thorough evaluation of possible conservation approaches, and the making of difficult decisions about their exhibition in a near future (probably in less than 50 years). Otherwise, the objects will become total losses, the museums will be full of PUR remains and these objects will be no longer presented to future audiences.

To find a solution, these subjects have been addressed in international debates focused on the conservation of contemporary art or on museum collections showing objects with non-traditional materials such as, scientific and ethnographic collections[108]. These initiatives have already resulted in important references[109] for the field of conservation, highlighting the relevance of both tangible and intangible values of an artwork when planning a conservation procedure. For that, the work developed by the art historian Alois Riegl (1858–1905) has been one of the most important references, as well as

[108] See for example, conferences such as 'Modern Art: Who Cares' (1997), 'Inherent Vice: The Replica and Its Implications in Modern Sculpture' (2007), 'Contemporary Arts: Who Cares?' (2010), 'A Arte Efémera e a Conservação: o Paradigma da Arte Contemporânea e dos Bens Etnográficos' (2010), and projects such as the 'International Network for the Conservation of Contemporary Art' (INCCA) (1999-) which has resulted in the project 'Inside Installations: Preservation and Presentation of Installation Art (2004–2007) and the most recent 'NeCCAR: Network for Conservation of Contemporary Art Research' (2012–2014).

[109] For example, 'Values and Heritage Conservation' (2000), 'New museum theory and practice: an introduction' (2006), 'Conservation Principles, Dilemmas and Uncomfortable Truths' (2009), 'A Arte Efémera e a Conservação: o Paradigma da Arte Contemporânea e dos Bens Etnográficos' (2010), 'Inside Installations: Theory and Practice in the Care of Complex Artworks' (2011), and 'Installation Art and the Museum: Presentation and Conservation of Changing Artworks' (2013).

the contributions of the preservation consultant, Erica Avrami[110] (Avrami *et al*., 2000). Riegl's definition of values and their attribution to objects (Riegl, 1903/1996) have become the support of conservation theories that reflect on what should be preserved. Accordingly, the conservator should pay attention to some specific aspects of the object depending on the values that are considered the most relevant in the particular case. Concepts such as authenticity, originality and re-interpretation have also been discussed in these debates, highlighting the fact that sometimes the conservator needs to think beyond the conservation of the original materiality in order to keep the creator's intention, the object's function or the object's significance, all based on careful assessment[111]. Hence, the discussion about ethical and theoretical dilemmas involved in the decision-making process for the conservation of artworks/objects is not new and 'Conservators today accept that objects change and that there is no one "pure" state' (Barker & Smithen, 2006: 87).

When the conservator deals with objects made of highly unstable materials and showing severe visual changes, the decision-making process is still difficult, mostly because there are no easy solutions and most degraded cases can lead to 'radical' decisions that are still poorly accepted within conservation. For PUR-based objects, the currently available active treatments can be considered too invasive or unable to restore the aesthetic value of the object. For that reason, conservators are (sometimes) 'obliged' to assume total losses, to display the object assuming degradation, or to replicate the PUR elements. While many studies have been addressing the particular problems rose by the presence of this polymer (especially as foam) in artworks[112], product design[113] and fashion (Morris & Keneghan, 2011), few focused on ethical discussions for the conservation of highly degraded PUR-based objects. As explained before, these discussions are particularly vital for conservators who are confronted with the wish to display contemporary iconic objects that unfortunately, show significant visual changes (which do not have proved solutions) or have collapsed due to the presence of ephemeral materials such as PUR. Although there is no perfect decision-making in conservation, the production of a jurisprudence based on similar cases and the sharing of experiences (from both conservators, visitors and the creators) may support future decisions involved in such demanding cases, as well as to alert to the necessity of discussions about this subject.

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[110] Erica Avrami is the Director of Research and Education at World Monuments Fund and professor in the School of Architecture, Preservation and Preservation at Columbia University.

[111] See for example, the model entitled, 'Significance 2.0: a guide to assessing the significance of collections', proposed by the *Collections Council of Australia* (Russell & Winkworth, 2009). This model identifies the values embodied by an artwork in relation to past, present and future generations. From this, future conservation measures are prioritised, ensuring that the decision-making process is carried out in order to better preserve the identified values and the object's significance.

[112] For example Guldemond (2005), Beerkens (2005), Rodrigo & Beerkens (2005), Jonge (2005), van Oosten & Keune (2005), Lorne (2005), Groot *et al*. (2013), van Oosten (2005), Cone (2008), Laganá *et al*. (2015), Royan, & Pellizzi (2015), and Langenbacher & Sommermeyer (2015).

[113] For example, Wickens (2006), Waentig (2008a), Melchar & Bamforth (2011), Groot *et al.* (2013), Fröhlich (2011), Graner & Lutz (2015), and Bozzo *et al*. (2015).

According to the provisions of the Portuguese Framework law governing the museums (Lei-quadro dos Museus Portugueses – Lei n.º 47/2004, de 19 de Agosto), Portuguese museums should define a conservation plan incorporating specific policies, guidelines and procedures for the conservation of their collections (artigo 28.º). In this plan, conservation strategies for more problematic cases such as PUR-based objects may be found. Consequently, this discussion may serve as a preliminary reflection for MUDE conservators for the definition of a conservation plan for objects containing ephemeral materials. This short discussion aims at contributing to the awareness of problems raised by the presence of PUR polymers in a museum collection and to discuss whether new paradigms could be involved in the conservation of contemporary ready-to-wear fashion and product design that suffer from their inherent vice in a short time. It also intends to debate both visitors' and authors' perception of objects showing degradation.

4.3.1 Reflections on decision-making for the conservation of PUR-based case studies from the MUDE collection

Before starting the discussion, a brief presentation of some degraded PUR-based objects (between 1999–2007) from the MUDE collection is given. Even though these objects surpass the time-period of this study (1960s and 1970s), they showed significant deteriorations in 2012. For that reason, their material characterisation[114] was carried out and PUR foams and TPU films were identified. As the presence of polyurethane was the cause of their degradation, these objects were included as case studies and selected for this discussion.

As examples of PUR foamed objects, a standing lamp (*Dark Light*, 1999) and a fashion accessory (bag strap, 2007) are discussed (Figs. 4.34 and 4.35).

The lamp, created by the French designer Jean Marie Massaud, showed a perfectly good condition in 2012. For this reason, the object was included in the permanent exhibition for a couple of months. After one month in open air display, the foam shade started to show structural weaknesses in one corner, leading to significant material losses (Fig. 4.34b). This led to the decision of removing the object. Due to the unusual appearance of the foam (large open pores) (Fig. 4.34b) and the fast degradation rate, the foam was analysed (as previously mentioned), confirming the presence of ester-based PUR foam.

[114] The material identification was carried out by infrared spectroscopy. For the cases in which it was not possible to collect samples (such as the interior foam of the bag strap), macro observations of the material and short inquiries to the designer indicated polyurethane.

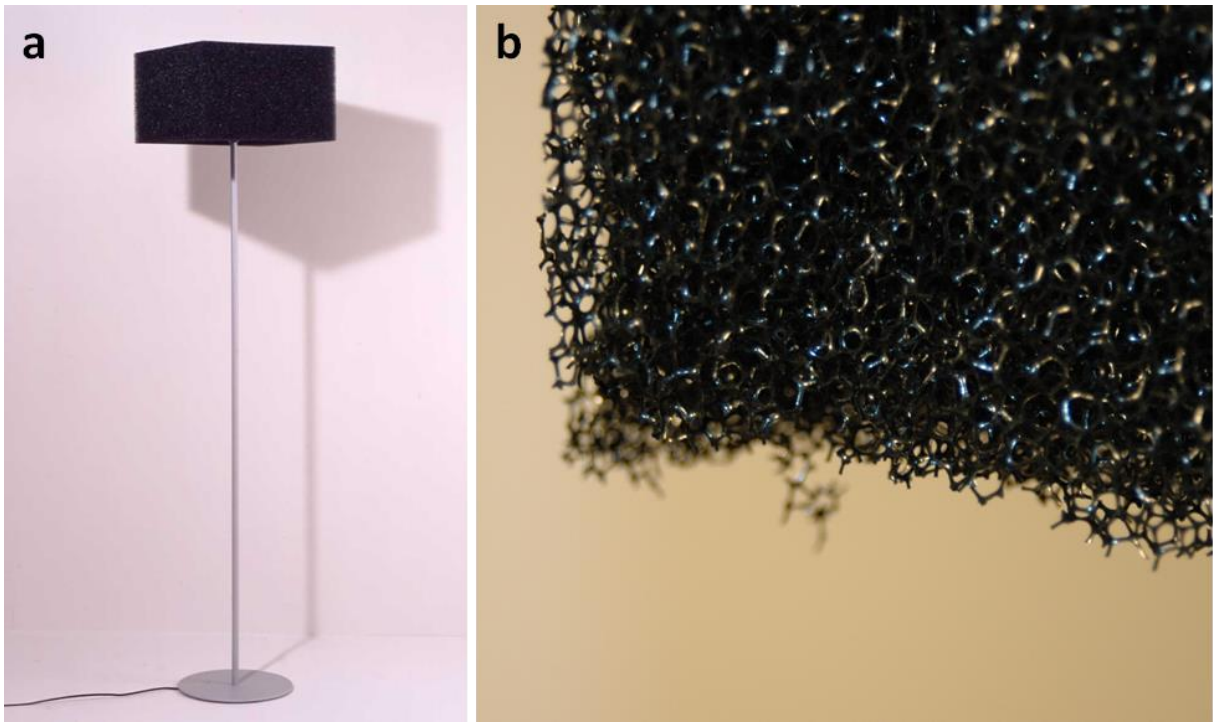

Figure 4.34 Jean Marie Massaud, *Dark Light* standing lamp, 1999. General view (a), and detail of the PUR quasi collapse foam from the lampshade showing material losses at the corner (b). Photos: © MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

Through the thoughtful collaboration of the Portuguese PUR foam processing company, Flexipol – Espumas Sintéticas S.A., the foam was identified as a PUR quasi collapse foam. These foams are characterised by large open pores, and are commonly used as air/water filters. Unfortunately, these foams have been left aside from conservation studies, probably, due to their low representation in museum collections or to the unawareness of their presence. Thus, the presence of a PUR-based object with this visual appearance was not posed by the museum's staff, let alone is composition based on ester-based PUR foam[115]. As previously mentioned, ester-based PURs are susceptible to hydrolysis, leading to the production of acid fragments throughout an autocatalytic process (van Oosten, 2011; Lattuati-Derieux *et al*., 2011). If the museum was aware of the object material nature, the lamp would not have been on display, especially because it is known that the RH inside the exhibition space can reach fluctuations of c. 30% in a single day (even though equipped with c. 5 air conditionings working 24h per day)[116]. Although the lamp was shortly removed after the detection of the first signs of deterioration, the foam collapsed after c. 2 weeks in storage (without light, with a temperature close

[115] As known, the use of ester-based polyols in PUR foam production has been decreasing since the 1970s due to their poor resistance to hydrolysis and the appearance of ether-based polyols as substitute. However, due to the lower cost of ester-based polyols, this PUR raw material continues to be used in foams which are supposed to assume temporary functions (e.g.: protective padding of cases or air/water filters).

[116] From the start of MUDE in 2009, the interior conditions of the museum were temporary and future works were being planned. At the moment, the museum is closed for works of integral rehabilitation.

to 21°C and a relative humidity of c. 50%)[117]. This situation shows how fast PUR degradation process can be and how in some cases conservators do not have time to predict ageing and establish preventive measures. Currently, this object is considered a total loss and the PUR remains are kept in the museum storage. Being the renowned French designer still alive (1966–) and taking into account the relatively recent production of the object (17 years ago), the museum's director is considering contacting the designer in order to discuss conservation possibilities. Perhaps, the replication of the foam shade should be considered, otherwise the object will be no longer displayable.

The bag designed by the Portuguese designer Miguel Rios was also showing a perfectly good condition in 2012, probably due to being protected by a disposable transparent film (as other three equal bags designed by Miguel Rios). For this reason, the accessory was included in the permanent exhibition (after removal of the plastic film) for four months in a showcase. During this time, nothing was registered. After the exhibition period, the bag was kept in the storage in open air (without light, T ≈ 21°C and a RH ≈50%) until a more appropriate place was being established for its conditioning. However, after c. 3 months in this space, the foamed strap became yellow (Fig. 4.35).

Figure 4.35 Miguel Rios, *System 2K07* shoulder bag, 2007. General view (a), non-exhibited bag strap (b) and exhibited bag strap for four months (yellowed) (c). Photos: © MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

[117] These values were measured with a data logger during one month.

This kind of foam, usually produced with aromatic isocyanates, is highly sensitive to light and oxygen (Shashoua, 2009b). Consequently, its discoloration can start in a few weeks after production due to the formation of coloured chromophores (Shashoua, 2009b)[118]. The designer explained that he observed this problem shortly after the first bags were produced (M. Rios, personal communication, January, 2012). Subsequently, he decided to use a different brand of foam, apparently of better quality. It is also known that Miguel Rios approached his previous clients and offered them a new bag strap. As MUDE's staff is aware of this change, what should be considered authentic in the case of this object? Which curatorial practice should be followed? Should the strap be replaced, or should the degraded one be exhibited? Perhaps both could be exhibited, with an explanation of the 'true' practice of design production, revealing both failures and successes? These are all questions with no easy answers, strongly dependent on institutional and cultural values and on the definition of authenticity for this object.

The last object selected for this discussion is a coat designed by the Belgian fashion designer Martin Margiela for the 1999–2000 Autumn–Winter collection (Fig. 4.36). According to the coat's label, the cover is based on a blended film of PVC and TPU (50/50). The presence of the PVC/TPU blend was confirmed in this investigation by IR spectroscopy, being the TPU based on ester-based polyols. Regarding its condition, yellow stains and spots are observed in localised areas of the coat (Fig. 4.36). Although these stains have significantly changed the visual appearance of the coat, material analysis did not enable to conclude the cause of their appearance. Since the museum's staff did not know what to expect from this piece in the future and the coat was already showing an undeniable change in its appearance (compromising its future exhibition), further research was carried out during this study. One of the first attempts was to contact the *Maison Martin Margiela.* Nevertheless, the request for collaboration through the answer of a short questionnaire[119] was denied and our doubts remain unanswered. For this reason, a deeper insight into previous studies concerning the degradation of these blends was carried out.

Few studies concerning the thermal and photo degradation of blends of PVC and TPU films were found (Piglowski & Laskawski, 1980; Osawa *et al*., 1994; Li *et al*., 2015), and none showed resemblances to this case. Still, some important conclusions described in the Osawa *et al*. study should be highlighted. As mentioned by the authors, 'the higher light absorptivity of the PU and the lower oxygen permeability of the PVC are responsible for the photodegradation behavior of the PVC/PU blends' (Osawa *et al*., 1994: 61). Osawa *et al*. reported that the photodegradation of the PVC/TPU blend is

[118] Since light was absent from the storage, yellowing was attributed to the free circulation and renewed presence of oxygen. According to other studies, yellowing of PUR in the dark has been observed and there are examples of PUR foams that have completely degraded to powder in the absence of light (van Oosten, 2011).

[119] For more details on the questionnaire, see Appendix II.

associated to the formation of polyene (from the PVC) and quinine-imide structures (from the TPU), as well as dependent on the diffusion of oxygen into the film (Osawa *et al*., 1994).

Figure 4.36 Martin Margiela, raincoat, Autumn–Winter 1999–2000 collection. General view (a) and condition of the TPU-based film in 2012 showing yellow stains (b). Photos: © MUDE – Museu do Design e da Moda, Coleção Francisco Capelo.

Since the most degraded areas of the Margiela's coat are characterised by yellow stains (Fig. 4.36), the formation of polyene and quinine-amide structures could be the cause of their appearance (increase of conjugated double bonds). For this reason, we have decided to build a polypropylene (PP) case with a transparent window in the cover for the packaging of the object. This enabled the monitoring of the stains without having to uncover the coat and minimised oxygen diffusion through the film. Apparently, the stains are becoming less clear. MUDE's director has not considered this coat a total loss, and before this study, the coat was displayed for 3 months showing the yellow stains. Regarding this option, it is also important to mention that it is possible that a different idea of the fashion designer's work was communicated to the public. According to Alessandro Masetti[120] and Laura Bradley[121], the Maison Martin Margiela (MMM) is recognised by the undeniable presence of the white colour (Masetti, 2012; Bradley, 2012). In the words of the MMM itself, this colour 'means the strength of fragility and the fragility of the passage of time', it is 'An expression of unity, purity and honesty' and 'It is never just white but more – whites – all the shades possible!' (Bradley, 2012). Accordingly, the

[120] Fashion expert and author of *The Fashion Commentator* blog.
[121] Commissioning Editor of *AnOther* Magazine and Website.

presentation of the A/W collection from 1999–2000, by the MMM, was characterised by the presence of a white decor where some oversized feather duvet coats were presented (Masetti, 2012; ModeMuseum Provincie Antwerpen, n.d.). Some of these coats showed transparent protective covers in plastic, which according to Laura Bradley, are commonly used by the MMM (Bradley, 2012). From this knowledge, and given the fact that the coat from the MUDE collection is a recent production (1999–2000), the deterioration found in this piece may not be perceived by visitors as damage. Consequently, the designer's work may be misinterpreted.

Similarly to these cases, conservators from other museum collections holding objects with new and currently, 'unknown' materials, may also have to face similar problems and the same lack of knowledge about their behaviour in long-term. From this perspective, several questions can be posed. What are the options for a museum with a large percentage of PUR-based design and fashion objects? Does it make sense to focus conservation practice on the object's original materiality?

In order to find a solution for these problems, many authors have been considering authenticity[122] as a powerful force in valuing heritage and in this way, a powerful tool to establish conservation priorities. On the other hand, authenticity is one of the most difficult concepts to define[123] and although this discussion does not intend to explore the definition of the concept, it intends to underline the complexity of the subject matter in ready-to-wear fashion and product design conservation and communication. In these two fields (product design and fashion), the definition of authenticity may pose a new challenge, possibly touching on some of the issues raised by contemporary art and industrial/scientific collections. With the attempt to clarify the concept in these fields, a brief discussion about the purpose of ready-to-wear fashion and product design has started during this study.

Although there are some theoretical studies focusing on design and fashion[124] and their communication in museums[125], to this discussion what matters is highlighting a number of characteristics associated to product design and ready-to-wear fashion that may help to understand the values embodied by these daily life objects. Later, curatorial practices for these objects are discussed.

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[122] See, for example, 'International charter for the conversation and restorations of monuments and sites' (1964), 'Languages of Art: An Approach to a Theory of Symbols' (1976), 'The Nara document on authenticity' (1994), 'The Declaration of San Antonio' (1996) 'Values and Heritage Conservation' (2000), 'Authenticity and Replication: The 'Real Thing' in Art and Conservation' (2014).

[123] By considering the definition of authenticity proposed by Lowenthal and Bumbaru, the conservator always has to keep in mind the subjectivity involved in this concept. As stated by the authors, 'authenticity is in practice never absolute, always relative' and 'is a temporary and contextual perception of the cultural values embodied by heritage' (Lowenthal, 1995: 123; Bumbaru, 1995: 281).

[124] See for example, Barnard (1998), Bürdek (2015), Sparke (2013) and Barnard (2004).

[125] See for example, Greff *et al*. (2008), Hall (2011), Melchior & Svensson (2014), Clark and De La Haye (2014), Pecorari (2012) and Hager (2012).

Ready-to-wear fashion, always influenced by historical, cultural and industrial contexts, implies a concept of multiple (as opposed to a unique piece), mass-production techniques and sometimes, the use of material novelties of the industry (Waddell, 2004). In addition, ready-to-wear fashion embraces a temporary character and an implicit 'disposability', which consequently, makes these pieces to be worn for a short period of time and never (in general) meant to last. Product design also entails similar qualities. According to Michael F. Ashby and Kara Johnson, design objects 'combine the functional with the symbolic and decorative', blending 'the technical with the aesthetic' and 'combining practical utility with emotional delight' (Ashby & Johnson, 2002: I). Consequently, these objects were meant to be used, experienced and sensed and can be described as commercial products. On the other hand, when they become part of a museum collection, most of the previous assumptions change, and these historical icons of furniture and apparel gain a new form of authenticity, functioning mostly as historical documents. In general, they are now seen as unique pieces, are no longer meant to be used and are expected to last in good condition. In most cases, keeping and displaying the original is the focus of conservation theory and practice. As MUDE collection holds some PUR-based objects showing poor and unacceptable conditions, how can conservation establish a strategy to keep communicating these objects, primarily produced to represent novelty? How can the museum keep what was intended to be temporarily functional?

If these objects are mass produced, the authors' hand is absent so they may be considered as 'not autographic' (Goodman, 1976: 124). By implication, authenticity might not be found in their original materiality. On the other hand, it is possible to confront this idea with the acknowledgement that, many times, the materials found in clothes and accessories are consciously and thoroughly selected by their authors. From this point of view, the preservation of the original materiality could be considered highly important, even though the author's hand is absent. As discussed in Chapter 2, the development of PUR revolutionised the world of ready-to-wear fashion and product design. With this novel material, it was possible to produce stretchable and fitting clothes (from the use of TPU fibres), comfortable and lighter shoes (from the use of foams), and stylish and elegant apparel (from the use of TPU coatings and films). Even today many PUR-based objects found in the MUDE collection could not have been produced with other material than PUR. Therefore, how can curatorial and conservation practices define a strategy for these objects?

By taking into account some conservation options and their further consequences on the authenticity of the objects, a diagram was created and four hypotheses were considered following the premise that PUR degradation is inevitable: apply an active conservation treatment, produce a replica, assume degradation or assume total loss (Fig. 4.37).

The first option is currently only applicable to PUR flexible foams, and more cases needed to be assessed. Even so, as foam degradation always implies considerable physical damage, treatments are

highly invasive and probably cause a change to the material matrix. Therefore, it is legitimate to question whether the original material is being respected and whether the aesthetic value is being restored.

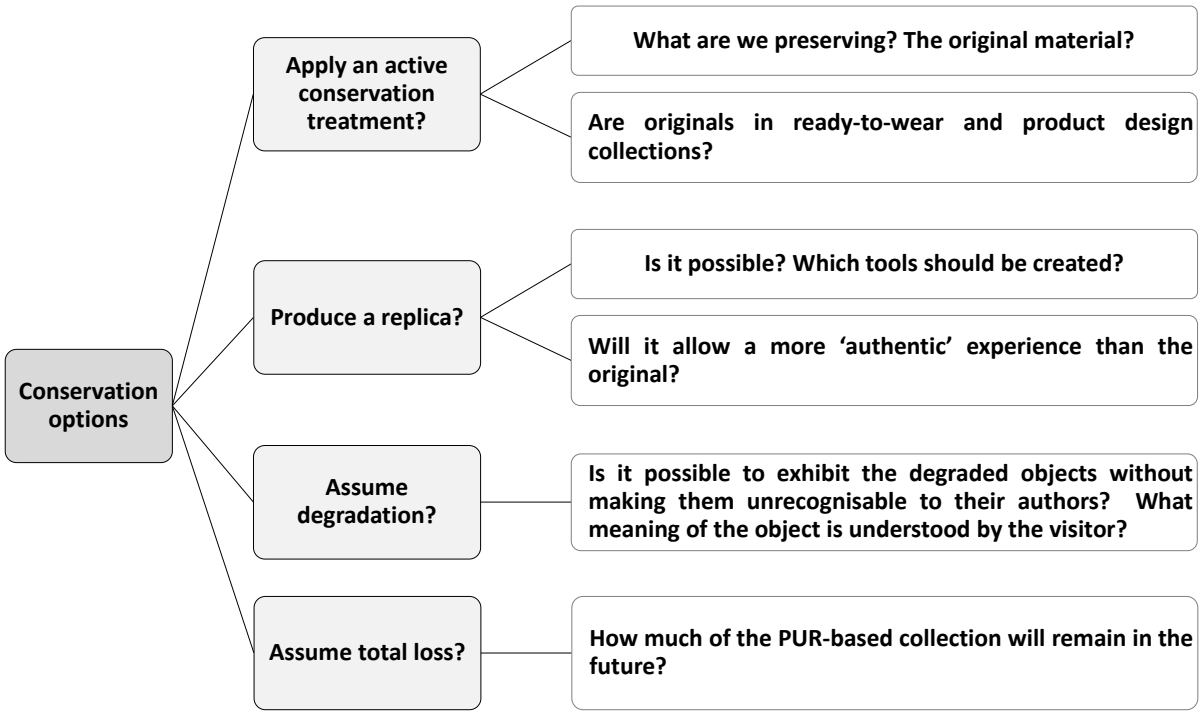

Figure 4.37 Schematic representation of four different options for the conservation of polyurethane-based ready-to-wear fashion and product design already showing degradation, and brief reflections on these options.

Regarding the second option, replication has been a major topic of discussion in the preservation of artworks and was the focus of a colloquium held at Tate Modern in 2007, 'Inherent Vice: The Replica and Its Implications in Modern Sculpture', which brought some highly degraded artworks to the attention of conservators. As Avrami *et al*. explain, it is important to emphasise that 'the ultimate aim of conservation is not to conserve material for its own sake but, rather, to maintain (and shape) the values embodied by the heritage' (Avrami *et al.,* 2000b: 7). On the other hand, replication is a controversial subject for 'those with an interest in the material evidence of the past' (Stanley-Price, 2009: 32), even when extremely degraded cases are being discussed. A large amount of documentation is required to produce a replica. Due to dynamic industrial production, it is hard to find the exact materials to produce an accurate replica. Information about technical features and procedures is needed and it is not always easy to obtain by interviewing the designer or by using common analytical techniques available in the conservation field. Furthermore, even if all these obstacles could be overcome, would the replica allow a more authentic experience than the original degraded object?

What are the costs and benefits? Sturtevant notes that replicas 'possess veracity but unfortunately eliminate the artist' (Sturtevant *apud* Mundy, 2007: 1). However, when design is the subject of conservation, the artist's hand may already be absent given the mass-production techniques. On the other hand, when a replica is created it supplants the original, turning it into a historical document of itself, especially when conservation deals with total losses (Cooper, 2007). According to the MUDE's director, it is not possible to apply the same rule to all cases, so case-by-case analysis should be adopted depending on the creator's intention and on the visual consequences of the degradation (B. Coutinho, personal communication, December 3, 2012). By starting to define the most important pieces in the collection, museum researchers should look for information that could identify whether degradation is changing the function of a piece beyond recognition by the author or by visitors familiar with the author's work. In most cases, the director prefers to preserve the immaterial meaning rather than keeping the conservation focus on the tangible aspects of the piece. This way, the exhibition of a replica (for highly degraded garments or for pieces in which degradation is masking the original intention) may be preferable when compared to the possibility of exhibiting the original object, as visitors would be able to appreciate the original appearance of the object, feel it or even try it on. However, the historical value would be lost, and in this case visitors could be disappointed and the purpose of the museum questioned. Due to the inherent instability of PUR the choice of materials to produce the replica may also raise important issues. If the same material is chosen (in this case, PUR), it will not take long for the replica to start showing signs of degradation. Instead a material with the same aesthetic and/or physical properties that is more stable than PUR could be chosen, if possible to find. However, despite the higher stability, this would lead to the original material choice being disregarded, and consequently the development of industry and its influence in design production. Other possibilities may be considered if additives are added to the production of the replica in which case PUR would become a plausible hypothesis as its lifetime could be extended. Furthermore, adequate storage and exhibition conditions would have to be adopted from the start. However, not only are material issues raised with the production of replicas but museums also have to consider management problems. If all these PUR-based objects became total losses, museums would be converted into collectors of PUR remains.

For the third alternative (assume degradation), if there is no information explaining the object's appearance, visitors may interpret degradation as the original look of the object and a false idea would be created. Also, the author may not recognise the object as his/her own production. Along these lines, authenticity may be reduced to historical value and the sense of novelty and aesthetic quality would be lost. Nevertheless, assuming degradation has been a common curatorial option at MUDE and the long blue jacket by Courréges (1971) is a recent example of that, as it was included in one MUDE's exhibition despite the recognised different appearance of the garment.

The last option, not to exhibit the object, would be a tragic decision. Not only would the museum become a collector of total losses as its purpose of heritage preservation and knowledge communication for future audiences would be compromised.

Regarding other museums experience in curatorial practices for contemporary product design and ready-to-wear fashion, some references were found[126], especially for fashion, which has been arising recent interest of researchers from the field. In these publications, important remarks were collected, which can be used as comparable examples for the establishment of a conservation strategy. For instance, Paola Antonelli[127] when confronted with John Thackara's statement[128], 'museums were bad news for design because they tended to foreground objects and products over the uses and relationships facilitated by them', stated that 'Museums are a real opportunity for design' (...) because they can 'get people to pause' (Antonelli, 2008: 86). On the other hand, some drawbacks were also mentioned by the curator. According to P. Antonelli, 'The biggest challenge with design shows is to avoid the "trade fair effect"', 'so people can distinguish between a museum and a trade fair or a normal store' (Antonelli, 2008: 87). As product design and ready-to-wear fashion are generally commercial products, conservation practices commonly used for art may not be practicable in these two contexts and conservation may also have to consider new approaches. When P. Antonelli was asked by Bennett Simpson[129] about changes in the practice of making design exhibitions, she mentioned that nothing has changed much in the past coupled decades (since the 1990s) (Antonelli, 2008: 87). However, still in her answer, P. Antonelli mentioned the importance of materiality for the visitor, when compared to virtual exhibitions.

> 'The materiality of the objects is almost a requirement. In some exhibitions, people can handle or use the objects. I remember the first time I saw this, at the Design Museum in London, which had and still has a very small collection that is mainly educational. It has all these famous chairs for people to try, and I thought that was fantastic' (Antonelli, 2008: 90).

Similarly, this strategy has also been undertaken by other museums holding fashion collections. An example is mentioned by Marco Pecorari[130] (Pecorari, 2014). According to his statement, the Mode Museum in Antwerp (MoMu) has been standing out in the last years by 'strategically employing a different way to think about fashion in museums' (Pecorari, 2014: 48). According to the author, in the exhibition 'Dream Shop' (2007), 'the public could actually try the designers' creations in fitting rooms

[126] See for example, Antonelli (2008), Hall (2011), Clark and De La Haye (2014), Graner and Lutz (2015), Melchior and Svensson (2014), Pecorari (2012, 2014), and Hager (2012).
[127] Currently, Paolla Antonelli is MoMA's senior curator of Architecture and Design.
[128] John Thackara is a writer, speaker and design producer, and director of *Doors of Perception*.
[129] Bennett Simpson is a senior curator at the Museum of Contemporary Art, Los Angeles.
[130] Marco Pecorari is a Doctor of Philosophy in Fashion Studies.

created within the exhibition hall' (Pecorari, 2014: 50). However, this confronts the typical display standards commonly required by conservation. On the other hand, perhaps conservators may need to start thinking about product design and fashion objects in a different perspective, establishing new strategies for their conservation, which in turn, may influence the way they are communicated to the public. Alternatively, different methodologies have also been followed. One example was discussed by Graner and Lutz when facing the need to restore a degraded design object (1969) for an exhibition (Graner & Lutz, 2015). Although the object suffered an extensive active treatment, its aesthetic appearance remained distant from the 'original' and the object was displayed assuming its degradation. The visitor's perception of the damages was discussed by the authors. Some of the posed questions were: 'Will they appreciate the value of this unique piece despite its visible degradation? And will they understand the condition as "patina" or as damage that should be repaired?' (Graner & Lutz, 2015: 49). After some discussions between conservators, museum's trustees, directors and curators, the current state of the object was accepted and appreciated by them, as well as used to 'educate visitors about the deterioration of modern materials' through the planning of guided tours focused on conservation (Graner & Lutz, 2015: 54). At the end, and as stated by the authors, this was 'one of the main attractions in the exhibition' (Graner & Lutz, 2015: 49).

In summary, two different perspectives were selected to be communicated to the public, one focused on the function and aesthetical relationship of design objects with the users (by letting visitors to touch and try the outfits), and the other focused on the historical value of the object (commonly adopted by museums). Either way, P. Antonelli also reported that the number of design exhibitions is very low, and because of that, there is no sufficient criticism (Antonelli, 2008) that probably, would help to build a conservation, curatorial and acquisition practice based on past experiences. Although this statement dates back to 2008, at the moment, there isn't an extensive research about this subject and therefore, museums continue to face the same difficulties when defining conservation strategies for contemporary fashion and product design objects showing degradation. When these objects comprise PUR, the posed challenges are higher and conservators and curators may need to find solutions in short time.

4.3.2 Collecting other conservation strategies

In order to help MUDE defining its own strategy for these objects, the gathering and production of documentation for the objects in discussion was aimed. Although libraries and archives were accessed, due to the objects recent production dates (1999–2007), it was observed that design and fashion history has not yet produced research about the making of these pieces, or even on the reasons that

led creators to use PUR over other materials. To overcome this lack, questionnaires were prepared[131] (see Appendix II) and sent by regular mail and/or email to fashion houses and product designers. Given the temporal proximity that enables contacting creators and production collaborators, the necessary and currently, non-existent documentation may be produced. However, this task was not successfully achieved because no answers have been obtained. On the other hand, as conservation and curatorial experiences for contemporary design and fashion objects showing degradation are still poorly explored in the literature, a questionnaire for museums was created in order to know if the same problems were being detected in similar collections (see Appendix II). From this approach, a positive outcome was obtained[132], and four answers from conservators and conservation scientists were collected. To complete this information, extended online surveys[133] were prepared to curators, conservators and researchers. These surveys were produced on the Google Forms platform and widespread through *LinkedIn*, *Conservation DistList* (Conservation Online, CoOL) and *ICOM-CC* forum of the working group *Modern Materials and Contemporary Art,* during c. one month. From this, 40 responses were obtained, including curators (4) and conservators (19) – all working in museums, as well as researchers and freelance professionals (17) – not working in museums. The respondents praised the initiative and positive comments were received. However, some flaws were also detected and due to the constructive criticisms of the respondents, the surveys can be improved for an eventual second phase. In general, this approach resulted in important information for the definition of the most central questions in PUR conservation and for the understanding of the solutions that are being considered and adopted by other museums. Even though only 40 responses were obtained, some of the issues reported have been described in the literature and are similar to the needs of PUR conservation in the MUDE collection.

None of the respondents attributed a lifespan higher than 50 years to PUR, regardless of its form or production date. And, although most of the respondents have identified climate controlled storages in their museums (UV filters, T ≈ 18–23°C and RH ≈45–55%), they have also reported their failure in the prevention of polyurethane degradation. This, once more, highlights the urgency of conservation studies focusing preservation and curatorial practices for this unstable material. Regarding the presence of total losses (due to the presence of PUR), almost half of the respondents have confirmed to have come across such objects (42%) and 32% named replication as a possible conservation approach (6 respondents). However, within the ones that have considered this hypothesis, only 1 has

[131] Questionnaires were divided into three sections: (1) introduction of PUR in the designer's work; (2) PUR acquisition and garment production; and (3) preservation options.

[132] Answers from Kim Verkens (conservator at MoMu – Fashion Museum of Antwerp), Meredith Montague (conservator at the Museum of Fine Arts, Boston), Brenda Keneghan (polymer scientist at the V&A Museum, United Kingdom) and Sue Gatenby (conservation scientist at the Power House Museum, Sydney) were obtained.

[133] See Appendix II for more information on the questionnaires and surveys, as well as the statiscal treatment of some of the the surveys' main results.

actually pursuit it, highlighting the difficult that is involved in such demanding task. Despite the wide acknowledgement of the problems arose by the presence of this polymer in museum collection, when the respondents were asked if they think that museum directors (in charge of collections with polyurethane objects) are aware of the short lifespan of this material, only 21% said yes. This highlights the fact that the knowledge and experience of conservators is still far from museum directors, which, in some cases (as Portuguese museums in general), may have a great influence in the definition of conservation strategies and policies for objects acquisition. Outside museums, conservators and conservation scientists/researchers (17 respondents) have also identified similar problems. From the point of view of curators, even though only four answers were obtained, an interesting perspective arose. Half of the respondents have said that there were times where their objects selection has changed in order to avoid the exhibition of polyurethane objects (probably due to their susceptibility to degradation); and three of the four curators (75%) confirmed the decision not to display a polyurethane object because of its degradation level. Either way, 75% have also confirmed to have displayed polyurethane-based objects assuming degradation. Contrary to the conservators' perspective (where almost 50% of the respondents have already considered a PUR-based object a total loss), in this case, only one curator has attributed this designation to a PUR-based object. This may be correlated to the material perspective commonly assumed by conservators, while curators may attribute a higher value to intangible aspects embodied in an object. Similarly to conservators, 100% of the curator respondents confirmed that museum directors are not aware of the short lifespan of this material. Regarding acquisition processes of PUR-based objects, one of the respondents (25%) confirmed at least one case where the degradation of polyurethane was the reason not to acquire a particular object. This stresses out the negative impact of PUR in artworks or historical objects, especially when entering museum collections.

In summary, although the problems faced by MUDE were identified among other museum collections, it was also observed that there isn't a wide dissemination and share of adopted curatorial and conservation decisions for this difficult material and for objects that suffer from inherent vice in short term (Wessel, 2008). As PUR is one of the most difficult polymers to preserve, both visitors and authors' perception of objects showing degradation should be more focused in conservation studies, as well as the focus of discussions inside museums.

4.4. Conclusions

The primary aim of this chapter is to assist in the conservation management of PUR-based objects in museums by supporting decision-making processes involved in their storage and communication to

the public in exhibitions. The first subject (storage) has been addressed by assessing an ageing experiment in the dark for PUR foams (ether- and ester-based) and TPU films (ester-based) under four storage conditions (open-air and enclosed at room T, low T and anoxic); and the second by discussing conservation strategies for contemporary PUR-based fashion and product design already showing degradation or considered total losses. This study has been able to expand the current (and deficient) knowledge about preventive conservation for PUR (identified in the *POPART* Project as a need), and to alert to an important and complex issue in PUR conservation that is, what might be the focus of conservation when dealing with PUR-based fashion and design that suffers from inherent vice in short term? Overall, new contributions for lowering the PUR high deterioration rate have been launched (by proposing promising storage conditions), and the production of documentation for an object has been highlighted as of fundamental importance for both the identification of values embodied in an object and definition of conservation strategies.

Open-air storage proved to be the most harmful condition, whereas, in general, anoxic storage showed the best results. Regarding the use of low T (≈12°C), beneficial results have been obtained. Still, this condition should be tested more and deeper. Concerning oxygen, the key role of this agent (independently of the PUR type) in PUR deterioration is stressed, which follows other results focused on synthetic materials. As stated by Yvonne Shashoua, current research indicates that 'the rates of crazing, crumbling and discoloration of natural rubber´ can be slowed in low-oxygen environments (Shashoua & Thomsen, 1993 as cited in Shashoua, 2009b: 198). Accordingly, and as supported by Shashoua, 'Since the degradation of most synthetic plastics involves reaction with oxygen, removing oxygen could be expected to limit the extent of the reaction' (Shashoua, 2009b: 198). In the case of PUR, this proved to be of imperative importance in the extension of its lifespan. Regarding the decision for enclosed packages (bags made of *ESCAL*^{TM} and aluminium barrier films), although previous research found that polyethylene can increase the migration rate of plasticisers from plasticised PVC, in this experiment (PUR), no evidences of extra damage attributed to these specific barrier films have been found. Conversely, simple enclosed packages proved to be enough to minimise colour changes (ΔE^*<2). Although the ageing experiment was limited to one year, unaged and naturally pre-aged references (commercial) have been included. Similar ageing tendencies have been observed, which extends the validation of the results to unaged but also aged objects, as the ones found in museum collections. Still, these results should be considered preliminary since longer periods and more degraded samples should be also tested. Raman spectroscopy has been proven to be an advantageous technique for the detection of early deterioration stages such as discolouration and possible changes into PUR intermolecular bonds (hydrogen-bonding interactions). Based on the monitoring of C=O stretching Raman bands assigned to urea and urethane linkages (1650–1800 cm^{-1}), hydrogen-bonding interactions on PUR structure have been monitored, and significant changes were detected upon

ageing. A correlation has been established between the broadening of the band at 1620 cm^{-1}, assigned to C=C from aromatic rings, and yellowing. Because changes in hydrogen-bonding interactions have been detected for samples stored in the dark, at room T and ≈50% RH, the high vulnerability of the supramolecular structure of PUR foams is highlighted. Moreover, the majority of the bands affected upon ageing are assigned to H-bonds. Because of their crucial role in the segregated structure of PUR, their instability is likely to result in significant changes in the physical properties of this material. In relation to the statistical data treatment, although the analysis of variance (ANOVA) has not been commonly applied in conservation studies (Reedy & Reedy, 1994; Dron *et al*., 2004), their application in this study resulted in the identification of significant correlations between visual aspects related to ageing (yellowing) and molecular fingerprints of the Raman spectra (changes in C=C stretching vibrations).

The second focus of the present chapter has also led to important remarks. One of the main conclusions is the importance of producing documentation. Documentation is essential to any conservation option in order to maintain a good memory of the object, plan a treatment or produce an accurate replica. It is impossible to make an informed decision without this background. As for the other raised issues, more questions were obtained than answers and once again authenticity was considered a complex concept to define. Considering the different values involved and the inherent subjectivity of its definition, along with the academic background of conservators and curators, a specific part or issue related to an object may be valued more than another. Another important observation is the question of whether it would be possible to extend the lifespan of the objects while retaining their cultural significance. Are the two compatible? Can we keep the original materiality and the intangible character of the object? Regarding PUR-based objects showing degradation, a decision must be made between exhibiting the original object and exhibiting the original purpose or aesthetic appearance. However, a casuistic approach is required not only for conservation reasons but also because of the risks involved in the possibility of replicating a large proportion of the collection. The conservator always has to strike a balance between the museum goal, purpose, creator's intention and the future preservation of the object. According to Stephen Hackney, 'if these important works are to be lost or to become unexhibitable, we need to find ways of interpreting them for future audiences' (Hackney, 2007: 2). When polyurethane heritage becomes the subject of conservation this sentence gains a powerful application. Conservation should make efforts to find solutions to these challenging issues by keeping in mind the most appropriate definition of the piece's authenticity and its future communication.

CHAPTER 5

CONCLUDING REMARKS AND FUTURE PERSPECTIVES

The research leading to the present thesis had as its primary purpose the enhancement of knowledge on the conservation of one of the most difficult synthetic polymers to preserve, polyurethane (PUR). With the aim of finding solutions to some of the particular issues raised by this polymer in museum collections, this work had as case studies PUR-based objects from *MUDE – Museu do Design e da Moda, Coleção Franscisco Capelo* (Lisbon, Portugal). Twenty-four PUR historical objects dated between the 1960s and 1970s were selected, including productions by European and American designers; and PUR foams (ether- and ester-based), TPU coatings (ester-based), and TPU fibres (ether-based). Part of these objects already show severe degradation after only a few decades since manufacture, which illustrates the demanding task of preserving modern and contemporary PUR-based fashion and design. The research explored different contexts of PUR in design, as well as the wide diversity of PUR forms, types, condition grades and ageing processes. In sum, it intended to react to the question 'What does the future hold for PUR fashion and design?', by pursuing the following main goals:

(i) To contribute to a more comprehensive biography of PUR during the time-frame of the present research;
(ii) To expand the knowledge on PUR natural ageing processes;
(iii) To accurately trace degradation in historical objects by using common assessment techniques in conservation science;
(iv) To propose a preliminary guideline for PUR long-term preservation in storage;
(v) To discuss management decisions involved in conservation and curatorial practices for PUR-based objects showing severe degradation;
From these main aims, this study intended to assist in the decision-making process of two important tasks in conservation: establishing preservation priorities for PUR-based objects in museums, and planning preservation and communication (display) strategies.
To achieve these main aims, inter- and multidisciplinary approaches have been followed.

5.1. Main findings of the study

Significant findings have resulted from the research work presented in this thesis. The following paragraphs describe the new contribution of this thesis to the current knowledge of PUR conservation.

Concerning (i), this goal has been achieved for national (Portuguese), German and Italian contexts; but industrial patents assigned to worldwide countries have been studied as well. This part of the research highlighted PUR as a revolutionary material in fashion and design (during the 1960s and 1970s), and most important, as a material which was consciously selected due to its own singular and unique

characteristics – increasing its value in the material culture of the second half of the 20th century. This research has also searched the particular work of Bayer (Germany) with renowned designers, and its investment in PUR-based design as a way to gain the consumer's trust regarding plastics. In this study, historical design icons from the MUDE collection are documented as testimonies of the industrial relationships established between PUR, the designers and Bayer. Regarding the Italian context, Gufram and Poltronova design companies were selected because of their unique work with PUR foams during the period under study, and the large number of objects by their authorships in the MUDE collection. It has been found that Gufram was created with the exclusive intention to work with PUR, whereas Poltronova intended to bring new forms and technologies to people's homes; yet, in both cases, PUR was described as a material to which it has been impossible to compete. Regarding the Portuguese context, this thesis searches for the first time the foundation of PUR industries in the country and the work of Portuguese designers with this material, placing Portugal on the map of PUR industries during the 1960s and 1970s. Along with this study, information regarding the construction of PUR design and fashion has been found, which, as known, is a valuable enlightenment about PUR material function and application in objects, and of fundamental importance during the survey of objects in museum collections. This part of the research enabled the national and European cultural valorisation of PUR use by industrialists and designers, and the recognition of its importance when found in design and fashion items. By accessing international patents, company archives and collecting testimonies, this study has been able to build a bridge between PUR production, history and technology, and between the material, the creator and his/her own design productions.

Regarding (ii and iii), the assessment of PUR from both historical objects and references submitted to ageing experiments has resulted in important findings for the field of PUR conservation. Common evaluation methods in conservation science (such as OM, and IR and Raman μ-spectroscopies) were selected, and both natural (outdoor) and artificial (photo-oxidation, λ>300nm, simulating indoor conditions) ageing experiments were carried out. From this approach, this part of the research proposes a visual and molecular pathway for PUR degradation, and assists the condition assessment of PUR in historical objects.

The outdoor ageing (even though less controlled) produced PUR degradation stages closer to the PURs found in the selected historic objects (good correlation). This better correlation may be related to the presence of higher and fluctuating RH levels, along with light. It has been verified that the presence of moisture may have changed the visual and the molecular ageing pathway of PUR (even ether-based), through the plasticisation of the HS domain; and the presence of light alone (artificial ageing, λ>300 nm) favoured the formation of carbonyl species in large scale (in both ester- and ether-based PURs). As conservation studies often carry out artificial ageing experiments to reproduce degradation as

found in historical objects, this research suggests that further studies into PUR ageing should consider not only the intensity and wavelength range of light, but also the presence of high (RH≥60%) and/or fluctuating RH in the assessment of PUR ageing. Ether-based PURs, for example, although commonly known for their susceptibility to light, are confirmed to follow a different molecular ageing pathway in the presence of fluctuating humidity (along with light), which is of primary importance in the reproduction of ageing conditions.

Polarised and fluorescence optical microscopies proved to be highly practical and valuable in (1) the observation of PUR visual damages at the micro level, and (2) in the recognition of the formation of different chromophores upon PUR yellowing. The first was easily detected based on reflected light under cross-polars (revealing micro holes, cracks and pitting); whereas the second was detected from the observed emission of different colours from samples showing different yellowing shades (by using both UV and Vis excitation lights). It is also important to emphasize that, to our knowledge, this study is the first to suggest which PUR molecular groups (amides bonded to aromatic rings) are responsible for PUR fluorescence sign. Therefore, OM was confirmed as an enlightening tool in the attribution of condition grades for PURs, even though it has been poorly explored in PUR conservation studies. OM also proved to be useful in the interpretation of spectral changes in both IR and Raman data. Due to the gathering of information from both visual and spectroscopic techniques, correlations between the two approaches were established, and fortunately, reproducible relationships were identified. This expands the potential of using OM in PUR condition assessment, which can be easily adopted in museums. Finally, reflected light microscopy under cross-polars might also be useful as an indicator of PUR foams polyol type (ether- or ester-based). This study has pointed out that aged ester-based PUR foams show a constant tendency to get extremely viscous upon ageing (remaining smooth and shiny under the microscope, even in severely degraded cases). Conversely, aged ether-based PUR foams tended to diffract light into different directions due to the high number of defects formed at the surface of the PUR cell buns (micro holes, minor cracks and pitting). As only visual signs are being assessed, this information can only be used as a first approach, and not as an accurate identification method.

In addition to the valuable use of OM, both infrared (diamond cell, transmission mode) and Raman μ-spectroscopies proved to be highly efficient in the detection of PUR molecular changes in samples exposed to both natural and artificial ageing experiments, as well as in objects from the collection. Their use as complementary techniques has also been shown, corroborating what has been mentioned in the literature. While IR μ-spectroscopy is confirmed as easily suitable for the acquisition of good resolution and reproducible spectra from PURs in poor and unacceptable conditions; Raman spectroscopy was more advantageous in the analysis of PURs in early stages of ageing (good and fair conditions). Along with these pros and cons, the elastic property of PURs (either foams, films or fibres)

proved to hinder the quality of IR spectra (in transmission mode) of samples showing good and fair conditions. Due to the quick recovery of the samples after compression (between diamond cells), the thin thickness achieved was lost only a few seconds after pressure release. On the other hand, and contrary to Raman spectroscopy, IR spectroscopy has enabled the spectral study of PURs in all condition grades – even though the less degraded samples required extra compression and a greater amount of time during the whole analysis procedure. Raman spectroscopy showed acquisition problems related to fluorescence. The fluorescence phenomena involved in this technique is confirmed to mask the signal-to-noise ratio of spectra collected from highly degraded and/or yellowed (brownish) PURs. On the other hand, Raman spectroscopy proved to be worthy of a greater focus in future conservation studies, especially in relation to the potential of using less energetic lasers (e.g. 1064nm). IR spectroscopy was identified as capable of detecting different molecular ageing pathways according to different PUR forms and types, and to distinguish production methods within ether-based PUR foams (e.g. slabstock and cold-moulded). As the wide class of PURs is undeniable (as reflected in the MUDE collection), the selection of a technique capable of detecting correlations between PUR variety of polymers and their ageing behaviour is of fundamental importance in conservation science. Another theme to emerge from this thesis is the importance of studying PUR as a supramolecular structure. As PUR hydrogen-bonding interactions were confirmed (by IR and Raman μ-spectroscopies) in this study to show strong changes upon ageing, PUR micro morphological structure has been proven to be highly susceptible to damage. According to the literature, these secondary bonds play a significant role in the design and preservation of PUR physical properties. However, and to our knowledge, no one has followed H-bonds over PUR foams natural degradation based on spectroscopic approaches. As this research detected significant changes on H-bonds in PUR samples stored in the dark, at room T and at 45–55% RH in less than a year, their high instability has been confirmed, as well as their possible relationship with the short lifespan of this synthetic polymer. Their monitoring proved to be of fundamental importance in the understanding of PUR as a supramolecular structure. Aside from this, the monitoring of the absorption band at c. 1640 cm^{-1} ($C{=}O_{urea}$ stretching) is proposed in this thesis as an IR ageing indicator of H-bonds level within PUR foams (following the proposal of other polymerisation studies), and as a marker for PUR condition assessment. This, along with the research work presented by Thea van Oosten, adds more information for the establishment of conservation priorities for PUR historical objects.

The findings discussed in (iv) have been achieved through the assessment of an ageing experiment in the dark for PUR foams (ether- and ester-based) and TPU films (ester-based) under four storage conditions (open-air and enclosed at room T, low T and anoxic). The results in Chapter 4 indicate open-air storage as the most harmful condition for PUR (even stored in the dark) since severe colour changes

and molecular degradation have been detected. Oxygen is suggested as a strong motivational factor for PUR (based on aromatic diisocyanates) yellowing (in the absence of light), independently on the PUR type (ether- or ester-based). Along with this important finding, the selection of simple enclosed packages (barrier films) has been proven to be enough to minimise colour changes in PUR foams ($\Delta E^*<2$) in the absence of light. This fact, as known, is of primary importance for the reduction of costs involved in museum expenses. As the acquisition of oxygen absorbers is highly expensive (along with the required purchase of barrier films) – especially for large volume objects – this research has confirmed that lower rates of PUR degradation can be achieved by placing the object inside a barrier film bag (under controlled humidity and T). It has also been confirmed that the rate of yellowing (Δb^*) in ether-based PUR foams is higher than in ester-based PUR foams, both in the absence of light. Thus, not only the chemical nature of the diisocyanate (aliphatic or aromatic) is a major influence in PUR yellowing (as commonly addressed in the literature), as the polyol type. Note that the two PUR foam references were both produced based on TDI, varying only in the polyol type. Apart from this evidence, Raman spectroscopy has also stood out as a valuable technique to translate early stages of PUR foam ageing into new molecular spectral lines. Conversely to IR spectroscopy, Raman has been able to show clear spectral variations in C=O and C=C stretching regions in samples that macroscopically did not show any clear sign of degradation. Furthermore, it detected H-bonds disruptions and was sensitive to molecular changes responsible for yellowing increase.

In sum, for the first time, contributions to the establishment of storage guidelines for PUR have been achieved and promising results were obtained to prolong the short lifespan of PUR. Furthermore, these measures can be immediately adopted by museum collections.

Concerning the subject described in (v), the challenges raised by the presence of PUR in museum collections have been analysed in this research from two different approaches: a brief review of published information regarding decision-making processes for the conservation (and communication) of highly degraded PUR-based artworks, fashion and product design; and the gathering of conservators' and curators' experiences with PUR conservation by an online and anonymous survey designed during this research (40 answers obtained).

It has been noticed that although PUR demanding challenges have been addressed in international conferences (since the 1990s) and scientific papers, the share and discussion of decision-making processes regarding severely degraded cases (or even total losses) are still poorly focused. This lack of information is especially observed in the following subjects: PUR-based objects considered total losses; replication or substitution of PUR elements; and visitors' and authors' opinions regarding such decisions as well as their perception of objects showing degradation. It has also been discussed

whether conservators may need to start thinking about conserving product design and fashion in a different way to art.

This thesis has attempted to discuss the "place" of authenticity in mass produced objects (in general), and whether new strategies should be adopted for their conservation, because, as is known, these strategies influence the way they are communicated to the public. In the case of PUR modern and contemporary fashion and product design clearly showing degradation, these discussions are especially urgent. There are no practical solutions capable of restoring their original aesthetic appearance, assuming degradation can change the purpose and significance of the object, and assuming that proclaiming total loss is a drastic decision.

The online survey enabled the addition of more information to these subjects. Even though only 40 responses were obtained, most of the reported issues have been described in the literature and identified as needs of PUR conservation within the MUDE collection. It has been observed that replication is not only being considered as a solution for PUR high conservation challenges, as sometimes adopted. Also, urgent areas of PUR future research in conservation have been stressed. One outcome from this survey was that museums are still acquiring PUR-based objects to incorporate their collections, even though their short lifespan is acknowledged. Consequently, there is an urgent need to produce the necessary tools to extend the lifetime of PUR and to find ways to preserve these important historical and artistic testimonies.

5.2. Limitations of the research

Concerning the contributions to PUR biography (i), although a worldwide overview was intended at first, this thesis has been primarily concerned with Portugal and specific companies from both German (Bayer) and Italian contexts (Gufram and Poltronova). The reasons behind this focus are related to the opportunity to access information, as well as to the availability of collaborators to share documentation and personal testimonies. Finally, the representativeness of productions from those companies in the MUDE collection is also high. The findings of the present study (in Chapter 2) are also mostly limited to product design, with less contributions to the history of PUR-based fashion. This lack was related to a greater difficulty involved in the collection of information about the subject, as well as to the almost inexistence of fashion houses working with PUR at that time, willing to share their experiences.

Regarding (ii), the main limitation was the production of references (unaged) capable of representing each PUR class as found in the MUDE collection. The selected criterion was to follow typical (with high commercial importance) PUR formulations of ether- and ester-based slabstock foams, ether-based cold-moulded foams and ester-based TPU films, and in this way, to extend the usefulness of the

obtained data to other museums and objects. Even though both infrared and Raman spectroscopies indicated similar chemical compositions between the case studies and the references, these techniques are not sensitive to compounds in lower percentages (<3%). Therefore, the findings discussed in Chapter 3 do not take in consideration the possible presence of additives (<3%) in the PUR formulation, which, as known, can influence the rate and pathway of PUR degradation. To get a molecular insight into the possible presence of additives in the selected PURs, Py-GC-MS could have been performed. The study of degradation products from PUR ageing (ii and iii) was also not intended in this thesis as this subject has been systematically addressed by authors such as Gardette, Wilhelm, van Oosten and Lattuati-Derieux. Thus, no further data was added in relation to this issue except for an in-depth IR spectroscopic study of H-bonds upon the ageing of PUR.

The findings on (iv) are limited to one year of ageing in the dark; therefore, the results should be retained as preliminary conclusions. The guidelines for the long-term storage of PUR discussed in Chapter 4 can only be used as promising measures, and if adopted, under careful monitoring. On the other hand, and to extend the validation of the results, unaged and naturally pre-aged references were tested, and similar ageing tendencies were observed, which supports the obtained results. As a last group of samples has been kept under the same tested conditions since 2014, further data could also be added in the future. Decreasing temperature should also be tested more and deeper, mostly because the potential irreversible damages brought by that measure are still poorly studied.

5.3. Future research perspectives

Future research on PUR conservation should focus on the wide diversity of this polymer class. Conservation science has been mostly focused on ageing studies and active treatments for PUR foams, leaving aside other important forms such as TPU coatings and fibres. Although foams can be the most commonly found PUR form in museum collections (also with the lowest lifespan), TPU coatings and fibres have been commonly used by fashion designers and industrialists, and are still lacking for urgent solutions, which at the moment, cannot be found in the literature. Furthermore, future research should also consider the different possibilities of PUR foam productions (slabstock, cold- and hot-moulded processes) as this thesis proved them to show different ageing behaviours upon the same ageing conditions. Regarding TPUs, there is an insufficient number of studies (or almost inexistent) focusing on their degradation, especially TPU-based artificial leathers and TPU fibres, which can be highly represented in fashion and textile collections. As they are highly susceptible to degradation, and stabilisation and consolidation studies are still missing, important historical testimonies produced with these materials can be lost in a near future.

The selection of ageing conditions, closer to the museum environment, is also suggested as a future trend to follow in the study of PUR ageing. This would allow more similar degradation stages to the ones found in historical objects and a more accurate trace of degradation. As the intrinsic instability of PUR to elevated T, RH and light is high, the selection of conditions distant from "real" environments can result in degradation signs that do not fall into the ones found in historical objects.

Based on the results of the present study, additional future research perspectives can be described. This research stresses the urgency of studies focusing on display conditions for PUR polymers as short periods such as 6 months can lead to severe damages on PUR. It also emphasises how the compromise 'Seeing versus Saving' is important when it comes to PUR communication to the public and how conservators do not know which measures should be adopted during the display of their PUR-based objects. As discussed before, even though room T, controlled RH (c. 50%), and values equal or lower than 300 Lux have been selected for PUR display, these were not capable to prevent its degradation. From the research work discussed in Chapter 4, displaying PUR-based objects in enclosed (e.g. glass cases) and/or anoxic conditions might be a solution, as oxygen (or the long-term availability of oxygen) was particularly stressed as one of the main causes of PUR yellowing, independently on the PUR type. Nevertheless, this possible solution is still caring for systematic research, in particular, the carrying out of studies discussing the exclusive role of light and oxygen in the discolouration of PUR foams.

Regarding the storage of PUR polymers, positive outcomes resulted from the present study. Nevertheless, these measures should be more tested, after longer periods of time and with larger and composite objects as found in museums. Severely degraded samples should be tested as well since enclosed packages might accelerate PUR degradation rate (especially when autocatalytic reactions are involved). Concerning the tested conditions, although the storage of PUR at 11°C showed positive results, this storage procedure should be tested more deeply, especially because lowering T in the object environments can lead to material stress and physical damage.

For the assessment of PUR ageing, this study suggests the possible potential of using fluorescence spectroscopy and FT-Raman, as PUR shows a strong fluorescence sign upon ageing (under the OM) and Raman proved to be worthy of a larger focus in the future. Another assessment technique to be further explored is the use of mechanical tests, which, as known, would give an insight into the physical properties of the material and would complement the spectroscopic data.

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APPENDICES

Appendix I - Experimental

I.1 Methodology

Following inter- and multidisciplinary approaches, this research brings together different methodologies from different fields of science and gathered primary and secondary sources. Libraries and archives were accessed; questionnaires, interviews and surveys were designed during this research (to museums, PUR industries and designers); unaged models (good condition) were prepared and/or requested to PUR suppliers (including PUR foams and TPU films); PUR-based case studies from the MUDE collection were selected (including different PUR types and forms, and different condition grades) and thoroughly studied; model samples were submitted to photo and outdoor ageing conditions to study different PUR degradation courses; the condition assessment of the selected case studies was carried out based on visual and molecular characterisation and finally, natural ageing in the dark was carried out in order to define the best storage conditions for PUR.

I.2 Questionnaires

Three different written questionnaires[134] were designed and sent to:

(i) International museums. General questions about the experience of museums (holding fashion collections) in PUR conservation were prepared and sent by mail to thirteen museums. This questionnaire was intended to share the conservation issues raised by the presence of PUR in fashion objects from the MUDE collection, and to be acquainted with conservation strategies adopted by other museums.

(ii) International fashion houses. General questions about the knowledge and experience of fashion designers who worked with PUR during the late 1960s were prepared and sent by mail to three fashion houses. This questionnaire was intended to produce documentation about the creative process of selected PUR-based garments in order to rethink conservation options and define a good conservation treatment for their future preservation.

(iii) International product design companies. General questions about the knowledge and experience of international product design companies who worked with PUR during the 1960s and 1970s were prepared and sent to three companies. This questionnaire was intended to give a new insight into the entrance and use of this material in the work of renowned foreign design companies.

[134] The questionnaires are shown in Appendix II.

I.3 Survey

Three extended online questionnaires[135] were prepared in order to collect answers from curators, conservators and researchers on PUR conservation. The questionnaires were produced on Google Forms platform and widespread through LinkedIn (conservation groups), Conservation DistList (Conservation Online, CoOL) and ICOM-CC forum of the working group Modern Materials and Contemporary Art, during c. one month. This survey intended to highlight the most central questions about PUR conservation and to define what are the main difficulties in the conservation of PUR. It also was intended to understand what solutions are being adopted by museum conservators, curators and/or directors, if replication is being considered and if not, what strategies are applied to extend the lifetime and the cultural testimony of PUR-based objects.

I.4 Informal interviews

Informal interviews were prepared and conducted with former and current workers from the PUR processing industry in Portugal, and with a national designer. These interviews were carried out by phone or in-person, and in some cases, answered in writing.

May 31st 2013 – Informal interview with Mário Veloso, former Production Director of Flexipol – Espumas Sintéticas S.A. Phone interview conducted by Susana França de Sá.

June 20th 2013 – Informal interview with Rodrigo Lencastre, current worker at the Commercial Department of Monteiro Ribas. Phone interview conducted by Susana França de Sá.

January 20th 2014 – Informal interview with Eduardo Afonso Dias, designer and colleague of Daciano da Costa at Metalúrgica da Longra. Personal interview held at MUDE – Museu do Design e da Moda, Coleção Francisco Capelo, in Lisbon and conducted by Susana França de Sá.

May 14th 2014 – Informal interview with António Pinto, former worker from Adico. Personal interview held at the facilities of Adico, in Avanca and conducted by Adelina Costa (director of Adico). The questions in the interview were designed by Susana França de Sá.

October 31st 2014 – Informal interview with Teresa Peixoto, current engineer at Monteiro Ribas. Personal interview held at the facilities of Monteiro Ribas, in Oporto and conducted by Susana França de Sá and Ana Maria Ramos.

[135] The surveys are shown in Appendix II.

I.5 Samples collected from case studies from the MUDE collection

Twenty-four PUR-based objects from the MUDE collection were selected as case studies (see Appendix III, Table III.1). This set includes national and international productions, as well as PURs showing conditions ranging from fair to unacceptable. Seventeen are made of PUR foams, five show TPU films or coatings and two are composed by TPU elastomeric fibres. From this set, a total of c. 70 samples (c. three per object/degradation pattern) were collected and characterised during this research. The objects are classified according to the condition scale proposed in the survey form designed by the European *POPART* Project: good, fair, poor and unacceptable (Lavédrine *et al*., 2012a: 297).

I.6 Additional case studies

Two ether-based PUR moulded foam artworks from a private collector and two ester-based PUR foams were included as case studies to add naturally aged references to the study of PUR degradation.

I.7 Materials

I.7.1 Unaged model samples

Slabstock foams

The production of the ether- and ester-based model samples was requested to Flexipol – Espumas Sintéticas S.A., following the typical specifications of water-blown slabstock foams.
The detailed information provided by the company was:

(i) ether-based PUR slabstock foam - TDI-80 diisocyanate (2,6- and 2,4-toluene diisocyanates), polyether-based polyols, 49.1 kg/m^3 foam density (ISO845), CLD 40% 4.5 kPa hardness (ISO3386/1) and 278 L/m^2/s air permeability (ISO9237).

(ii) ester-based PUR slabstock foam - TDI-65 diisocyanate (2,6- and 2,4-toluene diisocyanates), polyester-based polyols, 56.5 kg/m^3 foam density (ISO845), CLD 40% 7.8 kPa hardness (ISO3386/1) and 68 L/m^2/s air permeability (ISO9237).

Further infrared analysis[136] confirmed the use of polyether-based polyols mainly based on poly(propylene glycol) and polyester-based polyols mainly based on adipic acid-diethylene glycol polyester.
These foams were used as references of good condition (unaged) of polyether-based and polyester-based PUR slabstock foams.

Moulded foams – cold process

The production of the ether-based model sample was requested to Flexipol – Espumas Sintéticas S.A., following the typical specificities of water-blown moulded foams based on the cold process.
The detailed information provided by the company was: polyether-based polyols, blends of TDI/MDI diisocyanates and 50 kg/m^3 foam density (ISO845).
Further infrared analysis[137] confirmed the use of polyether-based polyols mainly based on poly(propylene glycol) and poly(ethylene glycol).
This foam was used as a reference of good condition (unaged) for polyether-based PUR moulded foams following cold processes.

Film

For the production of the model ester-based TPU film, *Estane® 5708 F4* was purchased from Lubrizol Advanced Materials. This product was selected due to its commercial importance within the synthetic leather industry. The detailed information provided by the company was: polyester-based polyol and MDI. Thin films were formed by dissolving pellets of *Estane® 5708 F4* in dimethylformamide (DMF) at room temperature (20% w/v). After complete dissolution, the solution was applied to glass slides using a metal spatula. The drawdowns were made inside frames made with five layers of scotch tape (previously applied) to keep the thickness of the films uniform. Evaporation of the solvent was completed in a vacuum oven at 60°C during 24 hours.
Further infrared analysis[138] confirmed the use of a polyester-based polyol possibly based on poly(1,4-butylene adipate).
This film was used as reference of good condition (unaged) for ester-based TPU films.

I.7.2 Naturally pre-aged model samples

[136] See Appendix IV.1 and IV.2 for more details.
[137] See Appendix IV.3 for more details.
[138] See Appendix IV.4 for more details.

Slabstock foams

A commercial PUR foam plate kept for ten years in indoor conditions and without any special care was used as a naturally pre-aged reference (poor condition) of ether-based PUR slabstock foam. This plate, primarily acquired for upholstery purposes, was selected for this study due to the high probability of following the typical processes of slabstock production and therefore, to serve as a comparison with the unaged model sample based on polyether-based polyols. Moreover, this reference shows an intense yellow colour and a fragile network clearly evident by the loss of flexibility and susceptibility to disintegration with handling. Further infrared analysis confirmed the use of aromatic diisocyanates (TDI) and polyether-based polyols mainly based on poly(propylene glycol). This foam was used as a reference of poor condition grade (naturally aged) for ether-based PUR slabstock foams.

A commercial PUR foam block, aged for c. 8–10 years without any special care and based on ester-based polyols was requested to Flexipol – Espumas Sintéticas S.A., following the typical specificities of water-blown slabstock foams. This block of foam shows a slight yellow colour. Further infrared analysis confirmed the use of aromatic diisocyanates (TDI) and polyester-based polyols based mainly on adipic acid-diethylene glycol polyester. This foam was used as a reference of fair condition grade (naturally aged) for ester-based PUR slabstock foams.

I.8 Instruments and methods

I.8.1 Sampling

Samples were collected per each selected case study and reference by using a Ted Pella micro tool, a scalpel and fibre optic light sources. The whole set of samples was stored between two concave glass slides, used as sample holders.

I.8.2 Sampling for optical microscopy

PUR Foams

Single cell buns of PUR foams (from references and case studies) were collected from the previous samples (section I.8.1) by using a Ted Pella micro tool and a scalpel under the stereomicroscope, Leica MZ16. Per PUR foam-based object, three independent cell buns were collected and analysed.

TPU-based leathers and films

As standard cross-sections in polyester resin were not possible to prepare (due to damages to the morphology caused during polishing), cross-sections of these materials (collected from case studies) were analysed between two glass slides (cut to 12.5 x 35 mm), with the sample surpassing the edge of the glass slides (used as holders).

TPU fibres

TPU fibres were analysed by placing the fabric or the single fibre between two concave glass slides.

I.8.3 Dark ageing

The natural ageing experiment was carried out in the dark, at 45–55% RH and during twelve months. In this ageing experiment, four storage conditions were assessed:

i) Open-air storage – samples kept in open-air, at room T;

ii) Enclosed storage – samples kept in sealed enclosures without oxygen removal, at room T;

iii) Cool-enclosed storage[139] – samples kept in sealed enclosures without oxygen removal, at 12°C;

iv) Anoxic storage – samples kept in sealed enclosures with oxygen removal, at room T.

PUR foam references were cut into several specimens of 4 × 4 × 1 cm and TPU films were used as described in section I.7.1.

Additional materials for the dark ageing experiment

For the enclosed systems, combined bags made of one side transparent ESCAL film and one side aluminium barrier film A 30T were used with the following specificities: ESCAL film - PP/ceramic deposited PVA/PE, 112 µm thickness, oxygen and vapour permeation (20°C) of 0.05 cm^3/m^2/day and 0.01 g/m^2/day, respectively; aluminium barrier film - PET/Al/LDPE, 120 µm thickness, oxygen permeation 0.01 cm^3/m^2day and vapour permeation < 0.04 g/m^2/day (40°C/90%RH) (Mitsubishi Gas Chemical Co., Inc., n.d.).

Humidity indicator cards from SÜD-Chemie Performance Packaging were used for the monitoring of RH inside each enclosed system (Süd-Chemie Performance Packaging, 2003). These cards show nine

[139] The term 'cool-enclosed storage' was adopted according to the definition provided by the *Image Permanence Institute*, 'A storage condition with temperatures usually between 45°F (7°C) and 60°F (16°C)' (Image Permanence Institute, 2017).

coloured squares which are cobalt chloride impregnated. The coloured squares respond to moisture in the air by changing colour. Each coloured square in the scale indicates a 10% humidity range, from dry to damp. The break between pink and blue squares shows the current RH.

For the anoxic storage, oxygen scavengers RP-K from Mitsubishi Gas Chemical[140] were used; these sachets are especially suited for organic materials since the RH inside each bag is not influenced; are based on silica and contain active charcoal for the adsorption of pollutants (SO_2, HCl or NH_3) (Mitsubishi Gas Chemical Co., Inc., n.d.). Oxygen indicators from Mitsubishi Gas Chemical were used to monitor the oxygen levels inside the sealed bags. These oxygen indicators turn pink below 0.1% oxygen and return to blue above 0.5% oxygen.

For each storage condition, open containers (8 x 8 x 2.5 cm) of polyester film from Melinex® were produced to prevent any direct contact between samples and packaging materials. The sealing temperature was around 150°C for 5 seconds.

I.8.4 Natural ageing (outdoor)

The natural ageing experiment was performed in outdoor environment for five months: sunlight (3–4 hours of direct sunlight per day), relative humidity ranging from 60 to 100% and temperature range between 5 and 20°C. In this experiment, samples were only protected from direct rain. For the outdoor and artificial ageing experiments, model samples were cut into several specimens of 2 x 2 x 1 cm.

I.8.5 Artificial ageing

The light ageing experiment was carried out using a CO.FO.ME.GRA 3000 light chamber equipped with a Xenon-arc light source (λ≥300 nm) (Fig. I.1), with constant irradiation of 800 W/m^2 and black standard temperature of 50–55°C ($T_{chamber}$≈25°C). The total amount of irradiance was 483 MJ/m^2.

[140] According to E. Coppolse, the composition of RP-K® is as follows: 10 to 40% > diatomaceous earth, 1 to 20% calcium hydroxide, 10 to 25% > unsaturated organic compounds, 15 to 35% > polyethylene and 10 to 35% inorganic absorbent (Coppolse, 2016: 5).

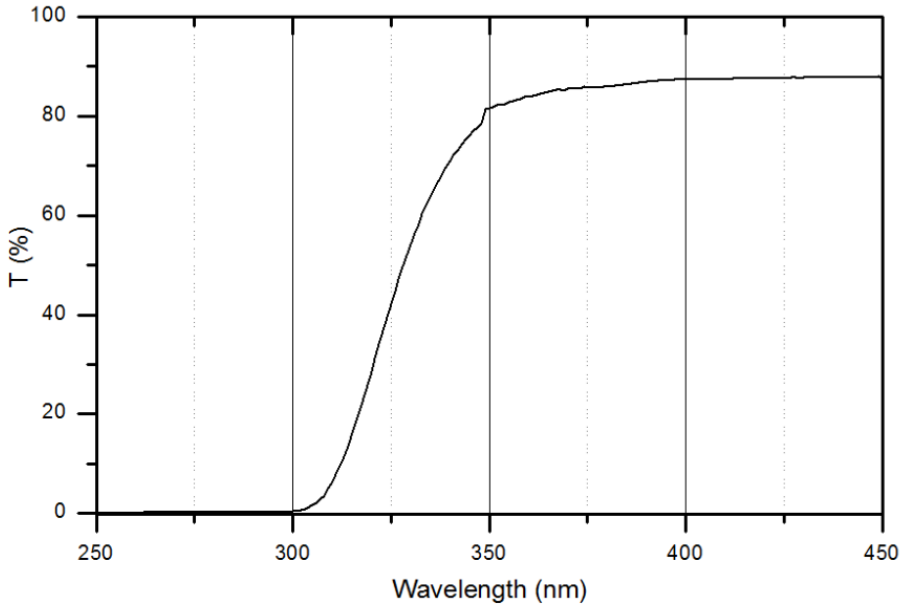

Figure I.1 Transmittance UV-Vis spectrum of the UV filter used during the artificial light ageing experiment.

I.8.6 Stereomicroscopy

To characterise the macro morphology of the samples upon ageing, stereomicroscopy images were acquired using Leica MZ16, coupled to Leica ICD digital camera, Leica Kl 1500 LCD fibre-optic light and Leica FireCam software.

I.8.7 Optical Microscopy

To characterise superficial changes, conventional and fluorescence microscopy images were acquired using a Zeiss Axioplan 2 Imaging system (HAL 100) coupled to Nikon DXM1200F digital camera and ACT-1 software. Different modes of reflected light illumination (darkfield, polarised light and UV light) were used to monitor changes in brightness, transparency, colour and texture of PUR foams, TPU films and TPU fibres, as well as changes in the outline morphology of the PUR foam cell buns. Moreover, the fluorescence behaviour of PUR foam cell-buns, TPU films and TPU fibres was followed. For the acquisition of fluorescence microscopy images, the samples were exposed to blue-violet light (Filter set 05 (Zeiss) - excitation BP 395–440 nm, beamsplitter FT 460 nm, emission LP 470 nm) and ultraviolet light (Filter set 02 (Zeiss) - excitation G 365 nm, beamsplitter FT 395, emission LP 420 nm)[141]. All fluorescence images were acquired under the same conditions, i.e., the intensity power of the UV-light source is fixed with all light parameters kept constant. When analysing the PUR foams

[141] BP: band pass filter; FT: 'farb teiler' filter, meaning color splitter filter; LP: long pass filter, G: gaussian filter.

cell-buns, all images were acquired by sampling and placing a single cell-bun between two microscope glass slides, one plane and another single concave. These single cell-buns were previously collected with a scalpel. Per foam, three independent cell buns were collected from the foam surface.

To get an in-depth analysis of the superficial changes of the PUR foam cell-struts submitted to 12 months of ageing in the dark, confocal microscopy images were acquired using an Olympus BX41 confocal microscope with the BXFM-ILHS microscope system and the Olympus LMPlanFL N 50x objective (50X, N.A.=0.50, W.D.=10.6mm, F.N.=26.5mm). These images were acquired under white light from the Euromex Fiber Optic Light Source EK-1 and without any previous preparation of the foam samples.

For the image acquisition of TPU fibres under transmitted plane-polarised light, the rotatable compensator Lambda (±8° 6 x 20 mm) was used, and single fibre filaments were cut into short pieces, which were placed on a glass slide with the addition of 2–3 drops of distilled water. A cover glass slip of a thickness matching the objectives was carefully mounted and air bubbles were removed gently.

I.8.8 Mass variation

Sample weight determinations were obtained with a Sartorius CP225 D micro analytical scale. Weight measurements were performed on the glass slide samples and PUR foams, mass variation was determined by comparison of samples aged in the dark (natural ageing experiment) with t=0h. Three independent measurements were performed per each sample.

I.8.9 Hardness variation

Samples hardness (Shore A) was measured with a HP Durometer (model HPSA, from Checkline Europe). The hardness value for each sample was calculated as the average of five independent measurements. Hardness variation was determined by comparison of TPU film samples aged in the dark (natural ageing experiment) with t=0h.

I.8.10 Colourimetry

Colourimetric measurements were performed using a *Datacolour International* colourimeter (*Microflash*). The optical system of the measuring head uses diffuse illumination from a pulsed Xenon-arc lamp over a 10mm diameter measuring area, 10° viewing angle geometry and D65 illuminant. Calibration was performed with bright white and black standard plates before each

measurement. Five independent areas were analysed (three measurements each) on the top of each foam specimen. To avoid any influence of the colourimeter weight in the flexible foam structure and consequently, in the final foam colour coordinates, a rigid structure of 10 mm height (same thickness as the foam samples), with a central square hole of 55 mm side was built. For the measurements, foams were placed in the central hole. In the case of the transparent films, colour was always measured on top of the calibration white tile in three independent areas (three measurements each). The average and standard deviation values for each *Lab** coordinates were calculated as well as the total colour variation (*ΔE**) according to the CIE 1976 formula (Equation 1). *ΔE** values above 2.3 were considered to correspond to just noticeable differences (JND) (Mahy *et al*., 1994).

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad \text{Equation 1}$$

I.8.11 Goniometer

Water contact angles (degrees) of the TPU films were measured with distilled water droplets using a CAM 100 goniometer (KSV Instruments) at room temperature. This measurement was carried out by capturing 10 frames (100 ms each). Each sample was measured in three independent areas.

I.8.12 Infrared spectroscopy

Infrared analyses were performed with a Nicolet Nexus spectrophotometer coupled to a Continuum microscope (15x) and a MCT-A detector cooled by liquid nitrogen. Infrared spectra were collected in transmission mode from 4000 to 650 cm^{-1} on micro samples compressed with a Thermo diamond anvil cell, 128 co-added scans and 4 cm^{-1} spectral resolution. Spectral analysis was performed using Omnic E.S.P. 5.2 and OriginPro 8 software and all spectra were baseline-corrected, normalised to C–C_{ar} absorption at ≈ 1600 cm^{-1} (identified as the most stable absorption during ageing) and the CO_2 absorption at c. 2300–2400 cm^{-1} was removed. The baseline correction was carried out as follows:

- Unaged reference of ether-based PUR slabstock foam, at 4000, 3700, 2500, 1870, 738 and 650 cm^{-1} absorption frequencies;
- Naturally pre-aged reference of ether-based PUR slabstock foam, at 4000, 3750, 1850, 955, 727 and 650 cm^{-1} absorption frequencies;
- Unaged reference of ether-based PUR cold-moulded foams, at 4000, 3700, 2500, 1870, 738 and 650 cm^{-1} absorption frequencies;

- Unaged reference of ester-based PUR slabstock foam, at 4000, 3700, 2550, 1825, 900 and 650 cm^{-1} absorption frequencies;
- Unaged reference of ester-based TPU film, at 4000, 3700, 2650, 1950, 877, 704 and 650 cm^{-1} absorption frequencies.

I.8.13 Raman microscopy

Raman microscopy was carried out using a Horiba Jobin Yvon LabRAM 300 spectrometer, equipped with a He-Ne laser 17 mW operating at 632.8 nm and coupled to the Confocal Microscope with high stability Olympus BX41. Spectra were recorded as an extended scan. The system was calibrated to better than 1 cm^{-1} using a silicon standard before the measurements. The laser beam was focused with an Olympus LMPlanFL N 50x objective (50X, N.A.=0.50, W.D.=10.6 mm). The laser power at the surface of each sample was 8.5 mW with the aid of the neutral optical density 0.3 filter. Three Raman spectra were collected on three independent points at the top of each sample. Raman data analysis was performed using LabSpec 5 software and all spectra were baseline-corrected for the following wavenumbers:

- Unaged reference of ether-based PUR slabstock foam, at 400, 686, 723, 989, 1220, 1505, 1570, 1748, 1800, 2700, 3150 and 3200 cm^{-1};
- Naturally pre-aged reference of ether-based PUR slabstock foam, at 400, 725, 992, 1014, 1226, 1500, 1744, 1800, 2700, 3150 and 3200 cm^{-1};
- Unaged reference of ester-based PUR slabstock foam, at 400, 685, 723, 1161, 1365, 1569, 1800, 2700, 3150 and 3200cm^{-1};
- Unaged reference of ester-based TPU film, at 443, 473, 556, 686, 1000, 1371, 1675, 1772, 1800, 2700, 2800, 3150 and 3200 cm^{-1}.

The spectra from the model ether-based PUR after six, nine and twelve months in the open-air were smoothed using a Savitzky Golay-Filter (Origin Pro8) for better spectral resolution due to increased fluorescence. For the ageing study, the Raman shift range from 1400 to 1800 cm^{-1} was selected and all spectra were normalized as follows:

- References of ether-based PUR foams, normalised to the C–H_2 bending vibration at c. 1455 cm^{-1};
- Reference of ester-based PUR foams, normalised to the C–H_2 bending vibration at c. 1447 cm^{-1};
- Reference of ester-based TPU film, normalised to the C–H_2 bending vibration at c. 1438 cm^{-1}.

These bands were selected because they were identified as the most stable absorptions through ageing. Band ratios for the 1660 cm^{-1}, 1700 cm^{-1}, 1712 and 1730 cm^{-1} wavenumbers (C=O stretching vibrations) were thus obtained; as well, the band width at half height (W) for the benzene ring

stretching vibration at 1620 cm^{-1} (only for the ether-based PUR foams) was obtained by fitting with a Lorentzian function. For all ether-based PUR foam spectra, the function fitting showed a coefficient of determination (R^2) higher than 0.95.

I.8.14 Statistical analysis

This approach was exclusively used for the assessment of the Raman data, angles (°) and hardness (Shore A) measurements from the dark ageing experiment.

The samples analysed by Raman spectroscopy were obtained in triplicate (three independent measurements) for each analysed wavenumber and the results were expressed as mean and standard deviation (SD). The same approach was carried out for the angles and hardness measurements in the TPU films. The mean values for the set of times (0, 1, 3, 6, 9 and 12 months) analysed were compared by analysis of variance (ANOVA) test. For each value (angles and hardness) and wavenumber analysed (1620 cm^{-1}, 1660 cm^{-1}, 1700 cm^{-1}, 1712 and 1730 cm^{-1}) when the overall result was statistically significant the Post-Hoc Tukey-Kramer multiple comparison test was conducted to identify which times were significantly different. The results from this test are shown as lower-case letters (ex. a, b, c) above the graphic bars. Times that are not statistically different have the same letter (and vice versa).

For the unaged ether-based PUR foam samples, correlation analysis was performed for all data between the band broadening (W) and the yellowing increase (using the b* coordinate from the CIELab colour space system) through the Pearson coefficient. All statistical tests were conducted by Statistica v.8 software (Statsoft Ibérica). Pearson correlation coefficient and significance differences were considered significant at a *p*-value below 0.05.

Appendix II - Questionnaires and survey

II.1 Questionnaires

II.1.1 Questionnaire sent to International museums[142]

Do you carry any of the following garments designed by André Courrèges, Roy Halston and/or Martin Margiela in your collection (see Table __[143])? If yes, please tell us which ones.

Do you carry different polyurethane garments by the same designers? (Look for spandex, elastane, Lycra or polyurethane in labels – polyurethane appears in a garment as foam, elastic fibre, synthetic leather or shoe sole, among other possibilities - please see Table __[144]). If not, please go to question__.

How do you identify the presence of polyurethane? (Experience, label, literature references or material characterisation)?

Do you carry any garments made of polyurethane elements? (Look for spandex, elastane, Lycra or polyurethane in labels).

Do any of those show evidences of polyurethane degradation (see Table __[145])? If yes, please mention which, degradation location, storage conditions (temperature and relative humidity, open/closed, with/without oxygen, with/without light, etc) and also if they have been displayed and for how long.

Based on your experience, which form of polyurethane do you consider to be the most unstable? Foam, fibre, rubber, coating, etc.?

Have you ever needed to make conservation decisions for those clothes? Why?

Have you ever considered replication for the PUR parts in those clothes? Why?

Have you ever done it? Why?

Do you have PUR-based garments and/or accessories that can no longer be exhibited (total losses)? Why do you consider them total losses?

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[142] The completed questionnaires are archived at DCR, FCT-UNL. A list of questioned museums is also presented.
[143] This table showed examples of fashion case studies from the MUDE collection.
[144] This table showed examples of PUR forms possible to find in fashion garments, shoes and accessories.
[145] This table showed examples of PUR degradation forms as found in fashion objects from the MUDE collection.

Table II.1 List of the international museums to which the questionnaire was sent

Museum	Completed the questionnaire	The museum holds PUR-based objects	The museum holds PUR-based fashion objects showing active degradation	The museum has considered replication/replacement for a PUR-based fashion object due to PUR	The museum holds PUR-based fashion objects considered total losses
Centraal Museum Utrecht, Netherland	No				
Fashion and Textile Museum London, UK	No				
FIDM Museum Los Angeles, USA	No				
Indianapolis Museum of Art (IMA) Indianapolis, USA	No				
Les Arts Décoratifs - Mode et textile Paris, France	No				
Mode Museum (MoMu) Antwerp, Belgium	Yes	Yes	Yes	No	Yes
Münchner Stadtmuseum Munich, Germany	No				
Museo del Traje Madrid, Spain	No				

Museum of Fine Arts (MFA) Boston, USA	Yes	Yes	Not specified	Not specified	Not specified
Philadelphia Museum of Art Philadelphia, USA	No				
Powerhouse Museum Sydney, Australia	yes	Yes	Yes	No	Not specified
The Metropolitan Museum of Art New York, USA	No				
Victoria and Albert Museum London, UK	Yes	Yes	Yes	No	No

II.1.2 Questionnaire sent to international fashion houses

Introduction of polyurethane in the fashion designer's work

How did André Courrèges[146] first know about the existence of polyurethane-based materials?

When did André Courrèges first use polyurethane in his fashion creations? (Look for spandex, elastane, Lycra or polyurethane in labels - polyurethane may appear in a garment as foam, elastic fibre, synthetic leather or shoe sole, among others).

Why did André Courrèges start to use this material? Why did he choose it? What were the advantages for him?

Did André Courrèges observe any kind of disadvantage when using polyurethane?

Polyurethane acquisition and garment production

Did André Courrèges go to industrial factories to find polyurethane? Or did he go to textile stores and warehouses?

Who used to work these PUR materials? The designer, his assistants or seamstresses? Did André Courrèges make his own "prototypes"?

Did André Courrèges have his own factory? Or did he look for industrial factories for his productions?

Did he have his own technology? Moulding, cut, etc.

In order to improve the documentation production would it be possible to give us access to some dated polyurethane samples used by André Courrèges in his garments?

Preservation concerns

Did André Courrèges know about polyurethane durability/resistance in the long term? If yes, was that a decision factor in his choice?

Do you still carry any André Courrèges garments? If yes, do any of those garments correspond to the ones shown in Table __[147]?

Currently, did you notice any kind of degradation in those garments (see Table __[148])?

Have you ever noticed degradation in other polyurethane garments designed by André Courrèges?

[146] In every question, the fashion designer's name was changed according to the recipient of the questionnaire.
[147] This table showed objects from the MUDE collection that were designed by the respective fashion authors.
[148] This table showed examples of PUR degradation forms as found in objects from the MUDE collection.

Have you ever needed to make a conservation decision for those clothes? If yes, please let us know which and why?

Is André Courrèges' House still producing the garments showed in Table __? If yes, what materials are you using? The same as always? If not, please let us know which and why did you decide to change.

Based on your experience, which form of polyurethane do you consider being the most fragile? Foam, fibre, rubber, coating, etc?

N.B. This questionnaire was sent to the fashion houses of André Courrèges, Roy Halston and Martin Margiela and no answers were obtained.

II.1.3 Questionnaire sent to international product design companies

Introduction of polyurethane in the company's production

How did Gufram[149] first know about the existence of polyurethane?

When did Gufram first use polyurethane in the production of its design pieces?

Why did Gufram start to use this material? Was a request from the designers? Was a company proposal? What were the advantages?

Objects' creative processes

Did Gufram go to specific designers to draw certain objects? What was the process? What was the idea behind their production? Did Gufram start with a drawing? Or did it start from material experiences?

Which materials did Gufram use in these two objects (see Table __[150])? What were the production techniques?

In order to improve the documentation production would it be possible to give access to some dated polyurethane samples?

Would you like to add anything more about the creative processes?

Preservation concerns

Do you know if Gufram's workers noticed any kind of disadvantage when using polyurethane?

What kind of information did (or do) Gufram have about polyurethane durability/resistance in the long term?

Does Gufram still carry any objects from the first decades of production? If yes, do any of those objects correspond to the ones showed in Table __[151]? Did you notice any kind of degradation in those objects (see Table __[152])?

Have you found degradation in other polyurethane-based objects produced at Gufram? What kind of degradation?

[149] In every question, the company's name was changed according to the recipient of the questionnaire.
[150] This table showed objects from the MUDE collection that were produced by the respective companies.
[151] Idem.
[152] This table showed examples of PUR degradation forms as found in product design objects from the MUDE collection.

Are you still producing the objects shown in Table __? If yes, what materials are you using? The same as always? If not, please let us know which and why did you decide to change.

Based on your experience, which form of polyurethane do you consider being the most fragile? Foam, fibre, rubber, coating, etc?

N.B. This questionnaire was sent to Gufram (Italy) and Poltronova (Italy), and to Vitra (Switzerland). Two answers were obtained (from Gufram and Poltronova), as discussed in Chapter 2.

II.2 Surveys

II.2.1 Survey to museum staff (conservator)[153]

Part I Sociographical Characterisation

What is your age?*[154]

____ years old

What is the highest level of education you have completed?*

- ☐ Less than high school
- ☐ High school/GED
- ☐ Some college credit, no degree
- ☐ Associate degree (2-year degree)
- ☐ Bachelor's degree (4-year degree)
- ☐ Master's degree
- ☐ Doctoral degree
- ☐ Professional degree (MD/JD)

What is your area of expertise (example: contemporary art documentation, synthetic materials, textiles, paintings, etc)*

_____

What type of museum collection do you work with?*
Select one or more options

- ☐ Art
- ☐ Product Design
- ☐ Fashion
- ☐ Toys
- ☐ Arts and Crafts
- ☐ Other _____

Part II Polyurethane material conservation

How do you identify the presence of polyurethane?*
Select one or more options

- ☐ Oral sources (author, production factory, etc.)
- ☐ Experience
- ☐ Tests (smell, feeling, chemical tests)
- ☐ Label
- ☐ Literature references
- ☐ Material characterisation. Please specify_____
- ☐ Other_____

[153] The completed surveys are archived at DCR, FCT-UNL. A compilation of most central results is also presented.
[154] (*) Mandatory question.

Which forms of polyurethane have you encountered in your collection?*
Select one or more options

- ☐ Foams (flexible and rigid)
- ☐ Coatings and adhesives
- ☐ Rubbers (soft and hard)
- ☐ Fibre

Which percentage of PUR-based objects in your collection shows degradation due to the presence of polyurethane?*
Select one option

- ☐ 0%
- ☐ 0% to 50%
- ☐ 50% to 100%
- ☐ 100%
- ☐ I haven't done a conservation survey on the polyurethane collection (go to question __)

When were these degraded objects produced?
Select one or more options

- ☐ 1950s
- ☐ 1960s
- ☐ 1970s
- ☐ 1980s
- ☐ 1990s
- ☐ 2000s

Which form of polyurethane have you found the most in your collection?*
Select one option

- ☐ Foams (flexible and rigid)
- ☐ Coatings and adhesives
- ☐ Rubbers (soft and hard)
- ☐ Fibre

Based on your experience, which form of polyurethane do you consider to be the most fragile/unstable?*
Select only one or two options

- ☐ Foams (flexible and rigid)
- ☐ Coatings and adhesives
- ☐ Rubbers (soft and hard)
- ☐ Fibre

Based on your experience, what do you think is the general lifespan of polyurethane?*
Select one option

- ☐ Less than 10 years
- ☐ 10 to 25 years
- ☐ 25 to 50 years
- ☐ 50 to 100 years
- ☐ More than 100 years
- ☐ Other_____

Have you ever been asked to carry out an active conservation treatment in a polyurethane-based object?*

- ☐ Yes
- ☐ No (go to question __)

What treatment have you been asked to perform?

- ☐ Cleaning
- ☐ Consolidation
- ☐ Coating
- ☐ Adhering
- ☐ Filling
- ☐ Other_____

Have you looked for supportive literature to carry out your treatment?

- ☐ Yes
- ☐ No (go to question __)

Have you found it?

- ☐ Yes
- ☐ No

Have you ever experienced a polyurethane-based object getting yellowed in the dark?*

- ☐ Yes. (please specify the form of polyurethane: foam, film, adhesive, coating, rubber, fibre)_____
- ☐ No

If yes, please mention the polyurethane chemical composition (polyether or polyester polyol and aliphatic or aromatic isocyanate) and its form (foam, film, adhesive, coating, rubber, fibre)

_____

What has been the storage condition for the PUR-based objects in your museum collection?*
If possible, please specify temperature, relative humidity, light, with/without oxygen, open/closed, packing material)

_____

Have these previously mentioned conditions have been successful in the preservation of the PUR?

- ☐ Yes
- ☐ No
- ☐ I don't know

Have you ever experienced degradation on PUR in short periods of display (less than six months)?*

- ☐ Yes
- ☐ No (go to part III)
- ☐ I never placed a polyurethane object on display (go to part III)

If possible, indicate the environmental conditions of the display (closed, open, T, RH, light, etc)?

_____

Part III – Research about polyurethane conservation

Are you aware of international research projects and scientific studies concerning the conservation of plastic materials?*

- ☐ Yes. If possible, could you specify (mention one or two)? _____
- ☐ No (go to part IV)

If possible, please mention one or two examples

_____

Do you access these studies to help you in the decision-making in plastics conservation?

- ☐ Yes
- ☐ No

In your opinion, are there enough scientific studies on polyurethane conservation (active and preventive)?

- ☐ Yes
- ☐ No
- ☐ I don't have an opinion

In your opinion, these studies are reaching those responsible for museum collections?

- ☐ Yes
- ☐ No
- ☐ I don't have an opinion

Based on your experience, which area in polyurethane conservation needs more study?
Select only one or two options

- ☐ None
- ☐ Active Conservation Treatments (cleaning, consolidation, impregnating, coating, adhering, filling)
- ☐ Preventive Conservation (storage, exhibition, packing and transport)
- ☐ Identification and characterisation of materials
- ☐ Assessment of polyurethane degradation
- ☐ Collection Surveys
- ☐ Other_____

Part IV Reflections on polyurethane's ephemeral nature

Have you ever came across a PUR-based object that had been considered a total loss?*

- ☐ Yes
- ☐ No (go to question __)

If possible, please indicate why was that object considered a total loss?

_____

Have you ever considered replication for a PUR-based object?*

- ☐ Yes
- ☐ No

Have you ever participated in any replication process for a PUR-based object?*

- ☐ Yes
- ☐ No

Do you think that museum directors in charge of collections with PUR are aware of the short lifespan of this material?*

- ☐ Yes

☐ No

Do you think that the lifespan of PUR is an ongoing problem in the conservation strategy of museums?*

☐ Yes
☐ No

Part V Administrative decisions on polyurethane objects

Have you ever participated in the decision making process of a PUR-based object acquisition/purchase in a museum?*

☐ Yes
☐ No (go to part VI)

Was the ephemeral nature of polyurethane a crucial factor in that decision?

☐ Yes
☐ No
☐ I don't know

Do you know of any case where the probable degradation of polyurethane was the reason to NOT ACQUIRE a new polyurethane object?

☐ Yes
☐ No

Part VI – Final (OPTIONAL)

If you want to leave a comment about any of the questions, please use the following space.

Thank you so much for your participation!

If you want to keep sharing your experience with us, please send an email to Susana França de Sá (email contact).

II.2.2 Survey to museum staff (curator)

Part I Sociographical Characterisation

What is your age?*[155]
____ years old

What is the highest level of education you have completed?*

- ☐ Less than high school
- ☐ High school/GED
- ☐ Some college credit, no degree
- ☐ Associate degree (2-year degree)
- ☐ Bachelor's degree (4-year degree)
- ☐ Master's degree
- ☐ Doctoral degree
- ☐ Professional degree (MD/JD)

What is your area of expertise (example: contemporary art, fashion, design, etc)?*
_____

What type of museum collection do you work with?*
Select one or more options

- ☐ Art
- ☐ Product Design
- ☐ Fashion
- ☐ Toys
- ☐ Arts and Crafts
- ☐ Other _____

Part II Polyurethane ephemeral nature

In the case of an exhibition, have you ever decided to change your objects selection in order to avoid the exhibition of polyurethane objects?*

- ☐ Yes
- ☐ No

Have you ever displayed a polyurethane object showing degradation?*

- ☐ Yes
- ☐ No

Have you ever decided to NOT DISPLAY a polyurethane object because of its degradation level?*

- ☐ Yes
- ☐ No

Have you ever defined a polyurethane object a total loss due to their degradation extent and/or loss of authenticity?*

- ☐ Yes
- ☐ No

[155] (*) Mandatory question.

Have you ever considered replication for a polyurethane object?*

- ☐ Yes
- ☐ No

Based on your experience, what do you think is the general lifespan of polyurethane?*
Select one option

- ☐ Less than 10 years
- ☐ 10 to 25 years
- ☐ 25 to 50 years
- ☐ 50 to 100 years
- ☐ More than 100 years
- ☐ Other_____

Do you think that museum directors in charge of collections with polyurethane objects are aware of the short lifespan of this material?*

- ☐ Yes
- ☐ No

Do you think that the lifespan of polyurethane is an ongoing problem in the conservation strategy of museums?*

- ☐ Yes
- ☐ No

Have you ever participated in the decision making process of a polyurethane object acquisition/purchase in a museum?*

- ☐ Yes
- ☐ No (go to part III)

Were there any divergent opinions in this process?

- ☐ Yes. If possible, explain the divergent opinions_____
- ☐ No

Was the ephemeral nature of polyurethane a crucial factor in that decision?

- ☐ Yes
- ☐ No

Do you know of any case where the degradation of polyurethane was the reason to NOT ACQUIRE a new polyurethane object?

- ☐ Yes
- ☐ No

Part III – Final (OPTIONAL)

If you want to leave a comment about any of the questions, please use the following space.

Thank you so much for your participation!

If you want to keep sharing your experience with us, please send an email to Susana França de Sá (email contact).

II.2.3 Highlighting the surveys' main results

The three surveys were produced on the Google Forms platform (based on an electronic survey form designed for Google Drive®) and widespread through *LinkedIn*, *Conservation DistList* (Conservation Online, CoOL) and ICOM-CC forum (Modern Materials and Contemporary Art working group). The surveys remained active for c. one month and have been filled in online by the respondents. The answers were totally anonymous and all data were automatically gathered in a database.

As shown in sections II.2.1 and II.2.2, mostly close-ended and mandatory (marked with *) questions have been designed for the survey. Open questions were included as well as the addition of the 'other' option in cases where several options were presented.

The surveys were exclusively directed to conservators, curators and conservation scientists who had already faced the specific challenges of conserving a PUR-based art or object. From this initiative, 40 responses have been obtained, by curators (4) and conservators (19) – all working in museums; as well as researchers and freelance professionals (17) – not working in museums (Fig. II.1).

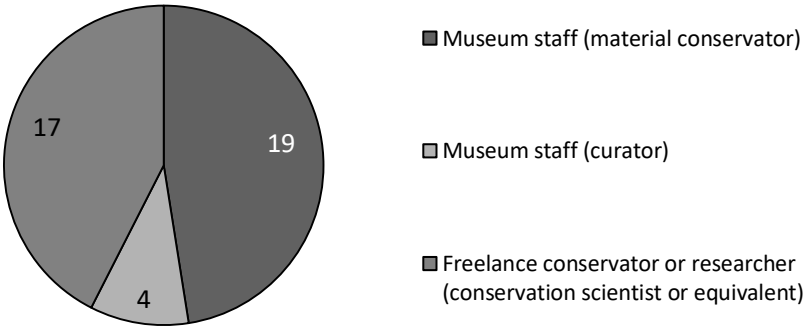


Figure II.1 Distribution of respondents (total 40) according to professional activity.

PUR in museum collections – generic observations

One of the first conclusions is the wide distribution of PUR polymers in museums declaring different types of collections: modern and contemporary art, arts and crafts, fashion (including shoes and accessories), product design, and toys – as expected; but also historical, technical, industrial and palaeontological collections[156].

[156] As described by the respondents, these collections can show transportation vehicles, audio, video, music instrument cases and even fossil replicas made of PUR polymers.

Within the set of PUR forms that can be found in such collections (foams, rubbers, coatings, fibres, and solids, among others), the respondents identified foams as the most common form (Fig. II.2)[157].

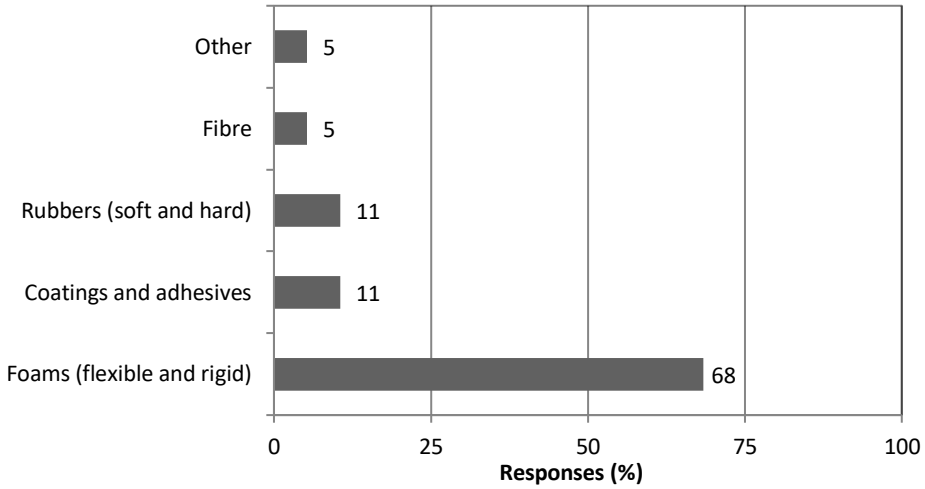


Figure II.2 Frequency of responses (by conservators working in museums) to the question 'Which form of polyurethane have you found the most in your collection?'.

Unfortunately, foams have also been identified as the PUR form most prone to deterioration, independently of their chemical composition (as this question did not take the chemical composition into consideration) (Fig. II.3)[158].

Regarding the general lifespan of PUR polymers, none of the respondents (both conservators and curators, working in museums) attributed more than 50 years to PUR (Fig. II.4)[159]. Even though it is known that this value depends on both intrinsic (e.g. chemical composition) and external (e.g. storage/exhibition conditions) factors of a specific material (and PUR is no exception), once more, this question was intended to be generic and to highlight the general opinion of the respondents about this synthetic polymer.

[157] The survey directed to both freelance conservators and researchers (not working in museums) highlighted the same generic tendency in the responses.
[158] Idem.
[159] Idem.

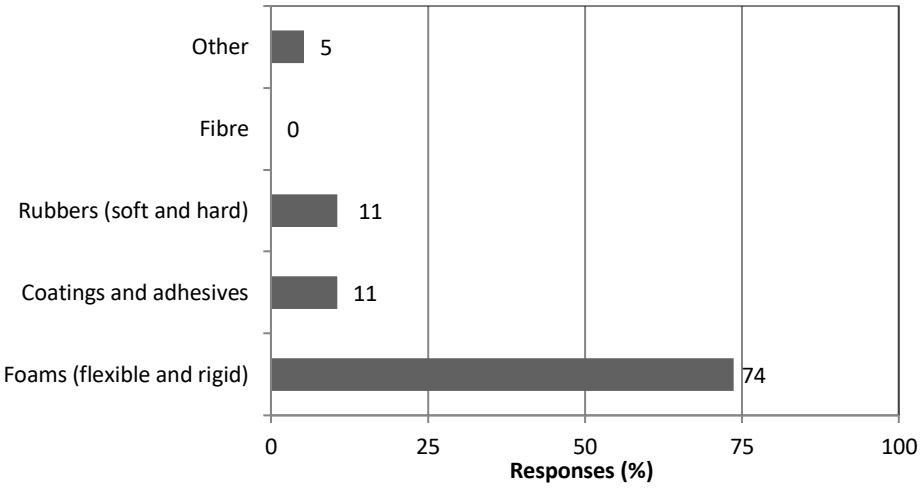


Figure II.3 Frequency of responses (by conservators working in museums) to the question 'Based on your experience, which form of polyurethane do you consider to be the most fragile/unstable?'.

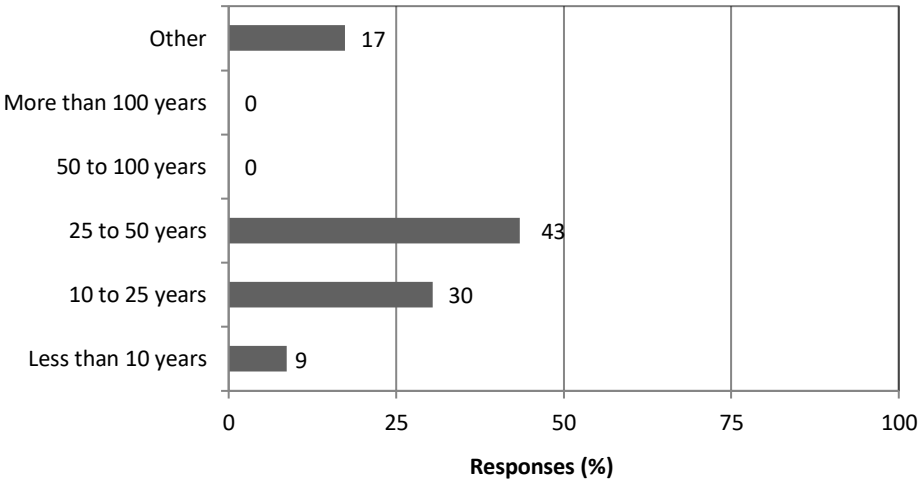


Figure II.4 Frequency of responses (total 23 – conservators and curators, both working in museums) to the question 'Based on your experience, what do you think is the general lifespan of polyurethane?'.

Storage and display conditions for PUR-based objects in museums

Interestingly, although most of the respondents have identified climate-controlled storage in their museums (no light, room T and 45–55% RH), some have also reported their failure in the prevention of polyurethane degradation (Table II.1).

Table II.1 Reported correlation between storage condition (described by the respondents – conservators working in museums) and efficiency in the prevention of PUR degradation

Described storage condition				Have these conditions been efficient in the prevention of PUR degradation?
No light	**Room T** (18–25°C)	**45–55% RH**	**Additional observations**	
✓	–	–	Closed with normal packing material	Yes
✓	✓	✓	Nearly perfect storage environment for textile	I don't know
✓	–	–	Either closed in a box or open	I don't know
✓	✓	✓	–	No
✓	–	–	Stored in archival quality boxes	I don't know
✓	✓	✓	With oxygen, covered in Tyvec	I don't know
✓	✓	35–75% RH	With oxygen, open	No
✓	✓	✓	Larger items (cars, computers, etc) in less controlled spaces	I don't know
–	–	–	Varies over time	I don't know
✓	✓	–	Open-air	I don't know
✓	✓	✓	Full climate control since 1960	No
✓	–	–	No environmental control, packed in open bubble wrap	No
✓	✓	35–65% RH	–	No
✓	–	–	Varies over time	I don't know
✓	✓	✓	–	I don't know
✓	✓	50–65% RH	with oxygen, open	No
✓	✓	✓	It is stored together with the textiles	Yes

(✓) yes; (–) not specified

Among the respondents who have already displayed a PUR-based object, c. 30% have experienced degradation in less than 6 months. Curiously, when the respondents were asked about to which display conditions PUR was exposed to (Table II.2), they reported values that did not fall far from the adopted guidelines (light, T and RH) for plastics (see Chapter 1). The majority of the respondents indicated values equal or lower than 300 Lux during display hours, room T and controlled RH (c. 50%). Still, these conditions were not capable of preventing PUR degradation during display for only 6 months (Table II.2).

Table II.2 Reported display conditions (as described by the respondents – conservators working in museums) for PUR-based objects that have suffered degradation in short periods of display (less than 6 months)

Described display condition				Were these display conditions efficient in the prevention of PUR degradation?
Light	**Room T** (18–22°C)	**45–55% RH**	**Additional observations**	
150–200 Lux	✓	✓	–	No
c. 200 Lux	✓	35–75% RH	Open-air display	No
No UV light Above 300 Lux	✓	✓	Closed	No
–	–	–	–	No
150–300 Lux	✓	✓	–	No

(✓) yes; (–) not specified

Access to research on PUR Conservation

One positive outcome from this survey was the acknowledgment that c. 80% of the respondents (within conservators working in museums) is aware of international research projects and scientific studies concerning the conservation of plastic materials[160]. Moreover, most of the respondents access these studies to make conservation decisions.

On the other hand, 68% have answered 'no' to the question, 'In your opinion, are there enough scientific studies on polyurethane conservation (active and preventive)?'. This stresses the lack of knowledge regarding the specific areas[161] of PUR conservation highlighted in Fig. II.5[162].

[160] As examples, the respondents identified the project to restore the Historical Collection of the Compasso d'Oro Award, the Future Talks conferences, the Forum Kunststoffgeschichte, the research work conducted by the Cultural Heritage Agency of the Netherlands (RCE), the *POPART* and the AXA Projects, publications such as 'Modern Art: Who Cares', the work of Fondazione Plart, and the conservation studies carried out by Waentig, Shashoua and van Oosten on plastics.

[161] The respondent was able to select one or two options at most.

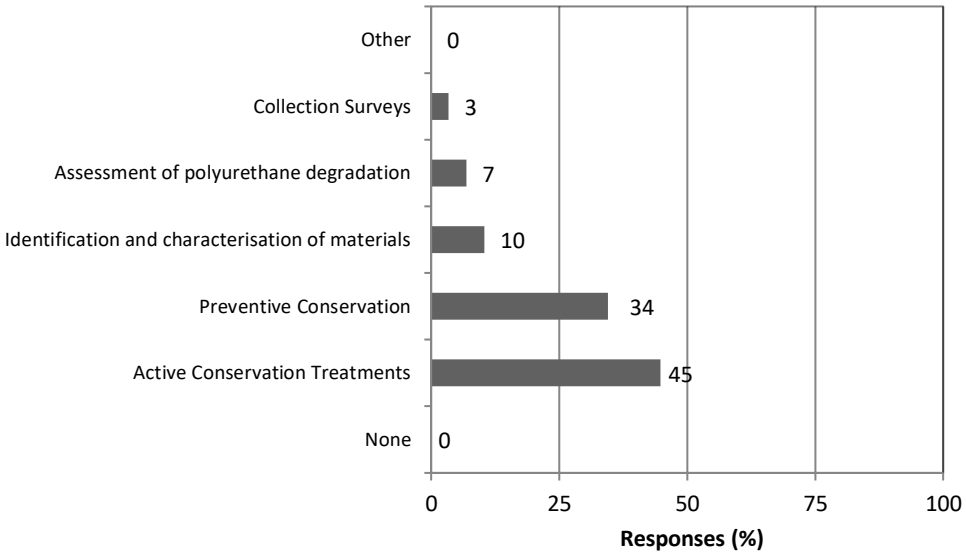


Figure II.5 Frequency of responses to the question 'Based on your experience, which area in polyurethane conservation needs more study?'. Preventive conservation included: storage, exhibition, packing and transport. Active conservation treatments included: cleaning, consolidation, impregnating, coating, adhering, filling.

Management decisions in PUR conservation and curatorial practices

As PUR is highly prone to degradation in few decades, the presence of total losses in museum collections due to PUR degradation has been covered in this survey. From this, c. 40% of the conservators (working in museums) have answered 'Yes' to the question 'Have you ever came across a PUR-based object that had been considered a total loss?*', and 25% of the curators (working in museums) have responded positively to, 'Have you ever defined a polyurethane object a total loss due to its degradation extent and/or loss of authenticity?' (Fig. II.6). Although the responses to the two different questions are compared in the same figure, it is possible to confirm that museums are currently facing management challenges of holding total losses due to PUR. The survey directed to freelance conservators and researchers (not working in museums) highlighted an even higher percentage for this subject matter, c. 65% of the respondents have come across a PUR-based object that was considered a total loss. From the respondents' answers to the question, 'If possible, please indicate why was that object considered a total loss?', one specific PUR form (degraded) has been reported repeatedly – foams. The respondents have described 'complete disintegration of foam', 'crumbling', 'totally pulverised foam', 'complete loss of its three-dimensional form' and 'formation of adipic acid' as reasons for this attribution (total loss) to an object. Unfortunately, all these situations

[162] The survey directed to both freelance conservators and researchers (not working in museums) highlighted the same generic tendency in the responses.

have no proven solutions with the exception of displaying the PUR foamed object 'assuming degradation' or to produce a replica (in order to avoid the designation of 'total loss'). Regarding the first option (to assume degradation), the question 'Have you ever displayed a polyurethane object showing degradation?' was only included in the survey directed to curators. However, an interesting perspective was collected. Although 75% of the respondents have said they had already displayed a PUR-based object showing degradation, 75% also reported that they had decided not to display a PUR-based object due to its high level of degradation. Moreover, when curators were asked 'In the case of an exhibition, have you ever decided to change your objects selection in order to avoid the exhibition of polyurethane objects?', 50% said 'Yes'. This emphasises the weight of PUR susceptibility to degradation when planning an exhibition and how, sometimes, the compromise 'Seeing versus Saving' has no easy solution.

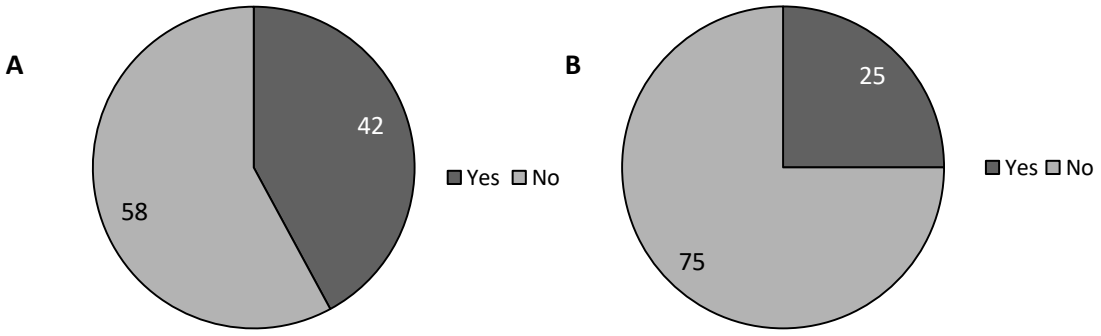


Figure II.6 Distribution (%) of responses by conservators (A) and curators (B), both working in museums, to a question about PUR-based objects considered total losses: 'Have you ever came across a PUR-based object that had been considered a total loss?*' (A) and 'Have you ever defined a polyurethane object a total loss due to its degradation extent and/or loss of authenticity?' (B).

Concerning replication, even though it has been considered a radical approach in conservation (see Chapter 4), 37.5% of the total respondents have already considered this approach to extend the memory of a PUR-based object. However, only five (12.5%) have actually participated in such a demanding task.

When the respondents were asked 'In your opinion, do you think that the lifespan of polyurethane is an ongoing problem in the conservation strategy of museums?', 80% of the total respondents answered 'Yes'.

In what concerns PUR-based objects acquisition/purchase for museum collections, only one of the respondents (in a total of 40) knew of one case where the probable degradation of PUR was the reason not to acquire a polyurethane object.

II.2.3.1 Considerations concerning the surveys' main results

From the respondents' answers, some considerations for the field of PUR conservation (such as, future research perspectives) can be drawn. Even though only 40 responses were obtained, some of the issues reported have also been described in the literature (see Chapters 1 and 4), and are similar to the needs of PUR conservation in the MUDE collection. For that reason, the results obtained might be used as suggestions for study areas to which PUR conservation should be addressed.

The high focus of conservation studies in PUR foams degradation and their consolidation (see Chapter 1) is easily justified by the large presence of such a material form in museum collections, along with its intrinsic instability after a few decades (as mentioned by the respondents). As confirmed in this survey, the respondents' lifespan attribution to PUR (10–50 years) is in accordance with the literature (van Oosten, 2011; Lattuati-Derieux *et al*., 2011), and there is no doubt for professionals that foams are definitely the PUR form that is more susceptible to ageing.

Regarding preventive measures, it can be concluded that the storage guidelines so far adopted in plastics conservation (Shashoua, 2009) are not satisfactory in the long-term assurance of PUR safety. This outcome, along with the identification of PUR storage as an urgent research subject by the EU *POPART* project in 2012 was the motto for the study presented in Chapter 4. The study (in Chapter 4) contributes to the definition of optimum conditions for PUR polymers (foams, films/coatings) and helps museums to make informed decisions in the establishment of storage procedures for these objects.

Similarly with the lack of proven solutions for PUR storage, some respondents have also stressed the same difficulties during the display of such objects. As observed in this survey, it is difficult to make decisions regarding the definition of exhibition conditions and time limits (e.g. months), especially because PUR degradation can be detected shortly after 6 months on display, even under "appropriate" conditions. As described before (Table II.2), even though room T, controlled RH (c. 50%), and values equal or lower than 300 Lux have been selected for PUR display, these were not capable of preventing its degradation. By taking these statements into consideration, some reflections about possible solutions can be posed. Although it is known that lowering T can slow the rate of degradation reactions (Michalski, 2002), the comfort of the visitor must be taken into

consideration, as well as both physical tensions and condensation that lowering T can cause to objects. Similarly, decreasing RH can also result in such damage. Accordingly, perhaps reducing light levels might be a solution for PUR safety during display, especially because ether-based PUR foams (also the most common PUR type since the 1970s) are known to be highly susceptible to photodegradation[163]. However, reducing light might not be plausible as the perception of objects can be changed. Although researchers such as Garry Thomson recommend 50 Lux for objects vulnerable to light damage[164] (Thomson, 1990), Stefan Michalski argues that these standards have been established based on visibility alone. As stated by the author, although it is true that 'We see most of what there is to see by 50 Lux', we also 'see objects not only slightly better, but differently with more light' (Michalski, 1990: 584). Accordingly, Kevan Shaw[165] states that 'The lower standard level of 50 Lux in museums is not acceptable in any field where any level of visual acuity is required' (Shaw, 1996: n.p.). Consequently, 'Our job is to explicitly predict the cost in deterioration', and not only on visibility (Michalski, 1990: 584). As polyurethane is highly prone to degradation in the short time, and the ether-type especially susceptible to light damage, the decision to display a PUR-based object should be carefully considered. On the other hand, to not display an object due to its material composition is also a drastic decision as museums may thus become collectors of total losses, or of objects that are not communicable to the public. From this perspective, this survey stresses the urgency of studies focusing on display conditions for PUR polymers and emphasises how the compromise 'Seeing versus Saving' (Michalski's webinar title in 2012) gains weight when it comes to PUR.

Concerning difficult decision-making processes in PUR conservation, it was observed that (in contrast to what was expected) replication is being considered (and sometimes adopted) as a solution for the high challenges posed by PUR conservation. A possible explanation for this might reside in the fact that when PUR is the subject matter of a conservation discussion, extremely degraded objects are often the motive behind the study. For this reason, such demanding cases as PUR may only find a solution in replication, even though replication has been considered a radical approach (Stanley-Price, 2009).

Another subject addressed in this survey has been the acquisition and purchase of PUR-based objects. As it has been confirmed that museums are acquiring PUR-based objects to their collections, it is urgent to produce the necessary tools to extend the lifetime of these important historical and artistic testimonies.

[163] Photoinduced modifications and breakdown of polymers such as polyurethane can occur due to exposure to light (Allen & Edge, 1992; Rånby and Rabek, 1992).

[164] Garry Thomson recommends 200/50 Lux illuminance levels for objects moderately (200 Lux) and particularly susceptible to damage by light (light fugitive) (50 Lux) (Thomson, 1990).

[165] Kevan Shaw is a lighting designer and his recent research has been focused on historical lighting and conservation.

In sum, the ephemeral nature of PUR is being discussed in museums, and conservators and curators are still in search of solutions that can be included in their collections management procedures.

Appendix III - Research case studies

III.1. Research case studies from the MUDE collection

Table III.1 Identification of research case studies from the MUDE collection

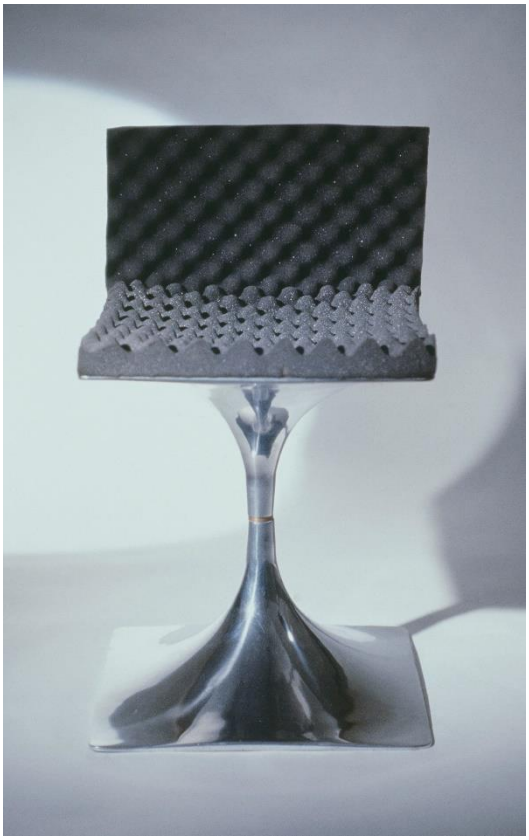
Form	Processing	Type	Case study		
			Author	**Title/Object**	**Date***
Flexible Foams	Slabstock	Ether-based	Roger Tallon	*Module 400* chair	1964
			Olivier Mourgue	*Djinn* sofa	1965
			Archizoom Associati	*Superonda* sofa	1966
			Archizoom Associati	*Safari* sofa	1968
			Pierre Paulin	*Amphys* sofa	1968
			Studio 65	*Bocca* sofa	1971
			Unknown	chair	1960s (?)
			Daciano da Costa	*Cortez* line armchair	1962
			Maarten Van Severen	*Blue Bench* sofa	1997
			Miguel Rios	*System 2K07* shoulder bag	2007
		Ester-based	Unknown (attributed to Paco Rabanne)	Jacket	c. 1960s
	Moulded	Ether-based	Peter Ghyczy	*Egg* chair	1968
			Gruppo Strum	*Pratone* lounge chair	1971
			Studio 65	*Capitello* armchair	1972
			Guido Drocco & Franco Mello	*Cactus* coat rack	1972
			Gianni Ruffi	*La Cova* nest	1973
	Reticulated	Ester-based	Jean Marie Massaud	*Dark Light* floor lamp	1999
Films/Coatings	n.i.	Ester-based	André Courrèges	Dress	c. 1965
			André Courrèges	Dress	c. 1970
			André Courrèges	Jacket	c. 1971
			Achille Castiglioni	*Primate* bench	1970
			Martin Margiela	Raincoat	1999/2000
Fibres	n.i.	Ether-based	Roy Halston	Swimsuit	c. 1976
			Roy Halston	Swimsuit	c. 1976

* design date; n.i. – not identified; (?) probable date

III.2 Case studies inventory form

Author	Title	Date	
		Design	Production
Roger Tallon (France, 1929–2011)	*Module 400*	1964	Éditions Lacloche: 1966–1975

Image



Dimensions	Label	Institution/Owner	Inventory number
64.5 x 38 x 38 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0375.01

Description

Chair made of metal and foam

	Location	Form	Type
Polyurethane	Structure	Foam	Ether (confirmed by IR μ-spectroscopy)

Author	Title	Date	
		Design	Production
Olivier Mourgue (France, 1939–)	*Djinn*	1965	Airborne International: 1965–1986

Image

Dimensions	Label	Institution/Owner	Inventory number
69 x 132 x 69 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0125.03

Description

Sofa in organic shape made of metal frame, red fabric and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Ether (confirmed by IR and Raman μ-spectroscopies)

Author	Title	Date	
		Design	Production
Archizoom Associati (Italy 1966–1974, Andrea Branzi, Gilberto Corretti, Paolo Deganello and Massimo Morozzi)	*Superonda*	1966	Poltronova: since 1966

Image

Dimensions	Label	Institution/Owner	Inventory number
38 x 240 x 100 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0130a MUDE.P.0130b

Description

Sofa in wave shape made of shiny and black fabric and foam

	Location	Form	Type
Polyurethane	Structure	Foam	Ether (confirmed by IR and Raman μ-spectroscopies)

Author	Title	Date	
		Design	Production
Archizoom Associati (Italy 1966–1974, Andrea Branzi, Gilberto Corretti, Paolo Deganello and Massimo Morozzi)	*Safari*	1968	Poltronova: 1968

Image

Dimensions	Label	Institution/Owner	Inventory number
62 x 260 x 217 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0133a MUDE.P.0133b MUDE.P.0133c MUDE.P.0133d

Description

Sofa made of plastic structure, leopard pattern fabric and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Ether (confirmed by IR and Raman µ-spectroscopies)

Author	Title	Date	
		Design	Production
Pierre Paulin (France 1927–2009)	*Amphys*	1968	Mobilier International: 1968 (?)

Image

Dimensions	Label	Institution/Owner	Inventory number
90 x 858 x 122 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0401

Description

Sofa made of metal frame, red fabric and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Ether (confirmed by IR and Raman µ-spectroscopies)

Author	Title	Date	
		Design	Production
Studio 65 (Italy, 1965–)	*Bocca*	1971	Gufram: since 1971

Image

Dimensions	Label	Institution/Owner	Inventory number
85 x 210 x 85 cm	*Gufram Multipli' 86 Bocca, 196*	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0134

Description

Sofa in lips shape made of elastic red fabric and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Ether (confirmed by IR and Raman µ-spectroscopies)

Author	Title	Date	
		Design	Production
Unknown	–	1960–64 (?)	Attributed to FOC: 1960s (?)

Image

Dimensions	Label	Institution/Owner	Inventory number
86 x 46 x 55 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	–

Description

Chair made of metal, wood structure, synthetic leather and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Ether (confirmed by IR µ-spectroscopy)

(?) probable date

Author	Title	Date	
		Design	Production
Daciano da Costa (Portugal, 1930–2005)	*Cortez*	1962	Metalúrgica da Longra: 1960s (?)

Image

Dimensions	Label	Institution/Owner	Inventory number
80 x 74.5 x 73 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.D0023

Description

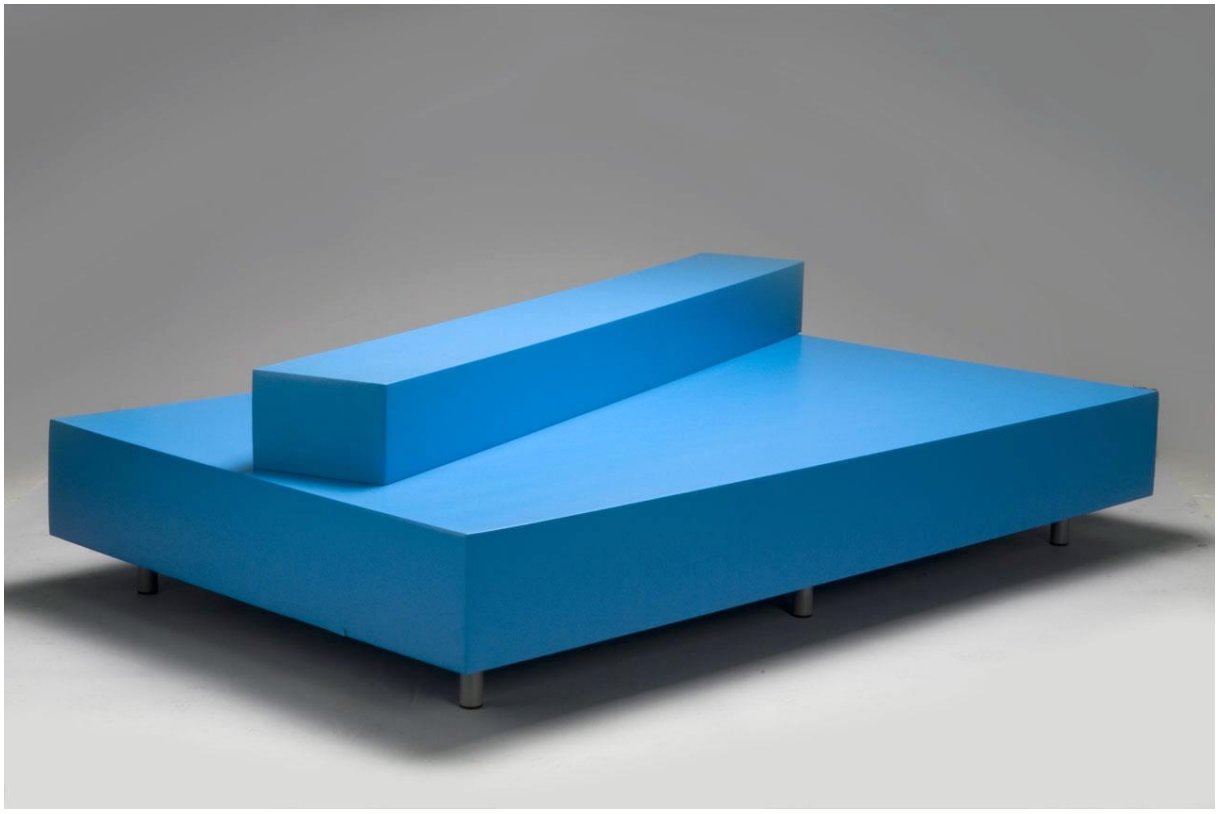
Armchair made of metal legs, wood structure, synthetic leather and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Ether (confirmed by IR μ-spectroscopy)

(?) probable date

Author	Title	Date	
		Design	Production
Maarten Van Severen (Belgium, 1956–2005)	*Blue Bench*	1997	Edra: 1997 (?)

Image



Dimensions	Label	Institution/Owner	Inventory number
200 x 124 x 53 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0672a MUDE.P.0672b

Description

Sofa made of metal legs and painted foam

	Location	Form	Type
Polyurethane	Structure	Foam	Ether (confirmed by IR and Raman µ-spectroscopies)

(?) probable date

Author	Title	Date	
		Design	Production
Miguel Rios (Portugal, 1965–)	*System 2K07*	2007	MR¯D: 2007

Image

Label	Institution/Owner	Inventory number
MRD	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.M.0709

Description

Modular shoulder bag made of synthetic fabric and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Not identified

Author	Title	Date	
		Design	Production
Unknown (attributed to Paco Rabanne)	–	c. 1960s	n.i.

Image

Label	Institution/Owner	Inventory number
44	Author of this dissertation for research[1]	MUDE.M.D0029

Description

Jacket made of metal foil, black lining fabric and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Ester (confirmed by IR µ-spectroscopy)

n.i. not identified

[1] In the beginning of this research this case study was part of Francisco Capelo collection (deposited in MUDE). However, in 2013, the object was offered by the owner to the author of this dissertation for research purposes.

Author	Title	Date	
		Design	Production
Peter Ghyczy (Hungary, 1940–)	*Egg*	1968	Reuter Product: 1968–1973 VEB-Synthese-Werk: 1973–1980 Ghyczy: since 2001

Image

Dimensions	Label	Institution/Owner	Inventory number
101 x 75 x 84 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0117

Description

Chair in ellipsoidal shape made of white plastic structure, green fabric and foam

	Location	Form	Type
Polyurethane	Cushion	Foam	Ether (confirmed by IR and Raman μ-spectroscopies)

Author	Title	Date	
		Design	Production
Gruppo Strum (Italy, 1963, Giorgio Ceretti, Pietro Derossi e Ricardo Rosso)	*Pratone*	1971	Gufram: since 1971

Image

Dimensions	Label	Institution/Owner	Inventory number
95 x 140 x 140 cm	*Gufram Multipli' 86 Pratone, 17/200*	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0212

Description

Lounge chair in grass shape made of green coating and foam

	Location	Form	Type
Polyurethane	Structure	Foam	Ether (confirmed by IR and Raman μ-spectroscopies)

Author	Title	Date	
		Design	Production
Studio 65 (Italy 1965–)	*Capitello*	1972	Gufram: since 1972

Image

Dimensions	Label	Institution/Owner	Inventory number
77 x 117 x 110 cm	*Gufram Multipli' 86 Capitello, 57/500*	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0123

Description

Armchair chair in classic capitel shape made of white coating and foam

	Location	Form	Type
Polyurethane	Structure	Foam	Ether (confirmed by IR and Raman µ-spectroscopies)

Author	Title	Date	
		Design	Production
Guido Drocco & Franco Mello	*Capitello*	1972	Gufram: since 1972

Image

Dimensions	Label	Institution/Owner	Inventory number
70 x 70 x 170 cm	*Gufram Multipli' 86 Cactus, 612/2000*	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0211

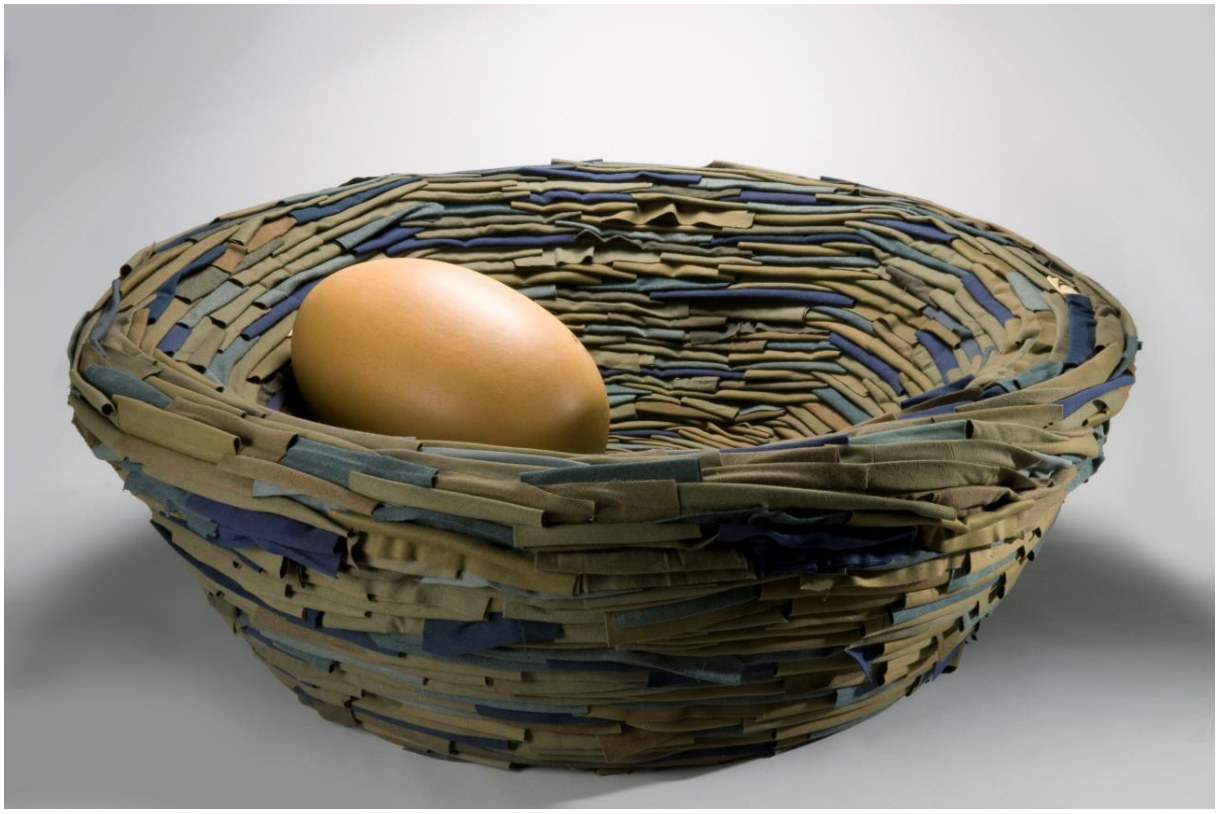
Description

Coat rack in cactus shape made of green coating and foam

	Location	Form	Type
Polyurethane	Structure	Foam	Ether (confirmed by IR and Raman µ-spectroscopies)

Author	Title	Date	
		Design	Production
Gianni Ruffi (Italy, 1938–)	*La Cova*	1973	Poltronova: 1973

Image



Dimensions	Label	Institution/Owner	Inventory number
75 x D195 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0327a MUDE.P.0327b

Description

Sofa in nest shape made of green, gray, brown and blue fabrics, foam structure and wheels; egg made of beige coating and foam

	Location	Form	Type
Polyurethane	*Egg's* structure	Foam	Ether (confirmed by IR and Raman µ-spectroscopies)

Author	Title	Date	
		Design	Production
Jean Marie Massaud (France, 1966–)	*Dark Light*	1999	Cinna: 1999

Image

Dimensions	Label	Institution/Owner	Inventory number
174 x 40 x 40 cm	*Dark Light made in France, Cinna*	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0515

Description

Floor lamp made of metal foot and foam lampshade

	Location	Form	Type
Polyurethane	lampshade	Foam	Ester (confirmed by IR µ-spectroscopy)

Author	Title	Date	
		Design	Production
André Courrèges (France, 1923–2016)	–	c. 1965	n.i.

Image

Label	Institution/Owner	Inventory number
Courrèges, made in France, Exclusively for Bonwit Teller *Wool 91%, Polyamide 1%, Acetate 8%, Cotton 50% Polyurethane 50%*	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE M.0368

Description

Blue dress with scalloped neckline, coated trim-leather and belt

	Location	Form	Type
Polyurethane	Trim	Coating in artificial leather	Ester (confirmed by IR µ-spectroscopy)

n.i. not identified

Author	Title	Date	
		Design	Production
André Courrèges (France, 1923–2016)	–	c. 1970	n.i.

Image

Label	Institution/Owner	Inventory number
Courrèges Paris Made in France	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE M.0372.01

Description

Brown dress with scalloped neckline, coated trim-leather and belt

	Location	Form	Type
Polyurethane	Trim	Coating in artificial leather	Ester (confirmed by IR µ-spectroscopy)

n.i. not identified

Author	Title	Date	
		Design	Production
André Courrèges (France, 1923–2016)	–	c. 1971	n.i.

Image

Label	Institution/Owner	Inventory number
Courrèges Paris, Made in France *Fabrique en France, Modele/Style: 17410* *Wipt with damp cloth only, Tissus Material,* *85 % Coton – Cotton, 15% Polyurethane Spandex*	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE M.0369

Description

Long blue jacket with belt

	Location	Form	Type
Polyurethane	Top fabric	Coating in artificial leather	Ester (confirmed by IR µ-spectroscopy)

n.i. not identified

Author	Title	Date	
		Design	Production
Achille Castiglioni (Italy, 1918–2002)	*Primate*	1970	Zanotta: 1970–1993 and since 1999

Image

Dimensions	Label	Institution/Owner	Inventory number
56 x 46 x 80 cm	–	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE.P.0148

Description

Kneeling stool made of metal, plastic base, artificial leather and foam

	Location	Form	Type
Polyurethane	Cover	Coating in artificial leather	Ester (confirmed by IR µ-spectroscopy)

Author	Title	Date	
		Design	Production
Martin Margiela (Belgium, 1957–)	–	Fall Winter collection of 1999/2000	n.i.

Image

Label	Institution/Owner	Inventory number
White Label PVC and PU (50/50)	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE M.0434

Description

Oversized raincoat made of synthetic film and inner feather duvet

	Location	Form	Type
Polyurethane	Top fabric	Film	Ester (confirmed by IR and Raman µ-spectroscopies)

n.i. not identified

Author	Title	Date	
		Design	Production
Roy Halston (USA, 1932–1990)	–	c. 1970s	n.i.

Image

Label	Institution/Owner	Inventory number
Halston	MUDE – Museu do Design e da Moda, Coleção Francisco Capelo	MUDE M.0579–0582

Description

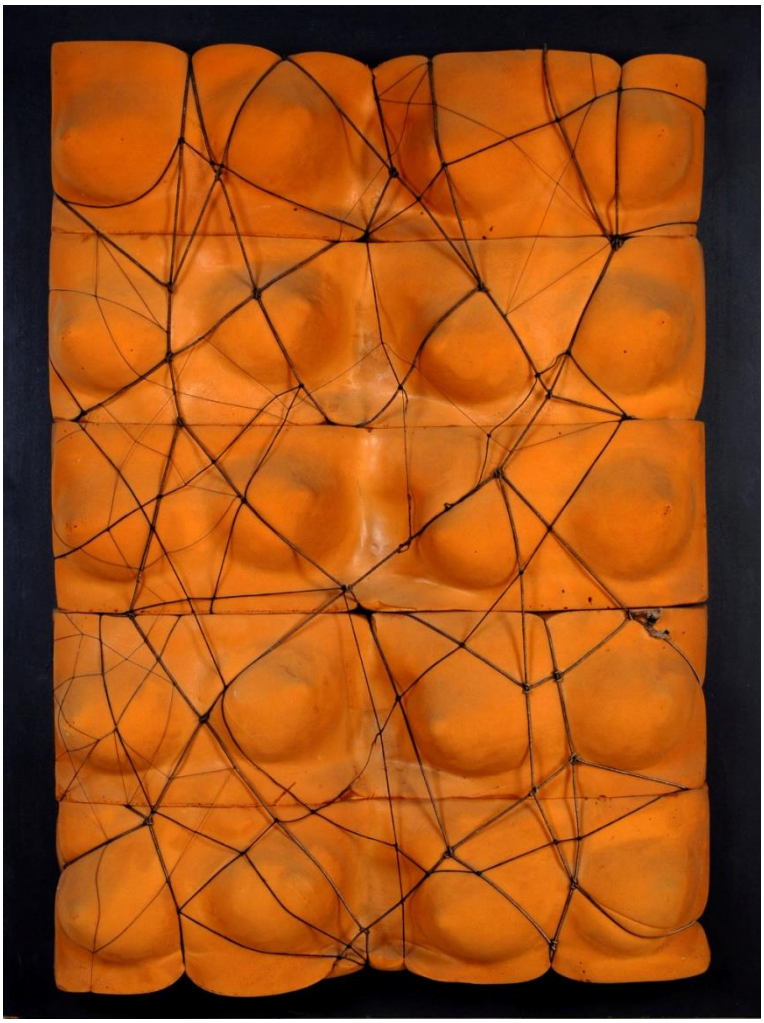
Swimsuits made of elastic dark blue fabric and white lining

	Location	Form	Type
Polyurethane	Top fabric	Elastic fibre	Ether (confirmed by IR μ-spectroscopy)

n.i. not identified

Author	Title	Date	Production
João Vieira (Portugal, 1934–2009)	*Viúva Negra*	1981	Flexipol – Espumas Sintéticas S.A.

Image



Dimensions	Signature	Institution/Owner	Inventory number
128 x 96 x 18 cm	–	Private Collection Ernesto de Sousa	–

Description

Sculpture showing Venus de Milo's breasts made of foam, covered by a network of threads and supported on a wooden board

	Location	Form	Type
Polyurethane	Breasts structure	Foam	Ether (confirmed by IR µ-spectroscopy)

Author	Title	Date	Production
João Vieira (Portugal, 1934–2009)	*A Nova Olímpia*	1981 (?)	Flexipol – Espumas Sintéticas S.A.

Image

Dimensions	Signature	Institution/Owner	Inventory number
23 x 79.5 x 17 cm	*A Nova Olímpia*	Private Collection Ernesto de Sousa	–

Description

Sculpture showing Venus de Milo's breasts made of foam

	Location	Form	Type
Polyurethane	structure	Foam	Ether (confirmed by IR μ-spectroscopy)

(?) probable date

Appendix IV – Infrared characterisation of the unaged models

IV.1 Ether-based PUR slabstock foam

TDI-80 diisocyanate and polyether-based polyols mainly based on poly(propylene glycol)[166] (Fig. IV.1). The assignment of the main IR bands is shown in Table IV.1.

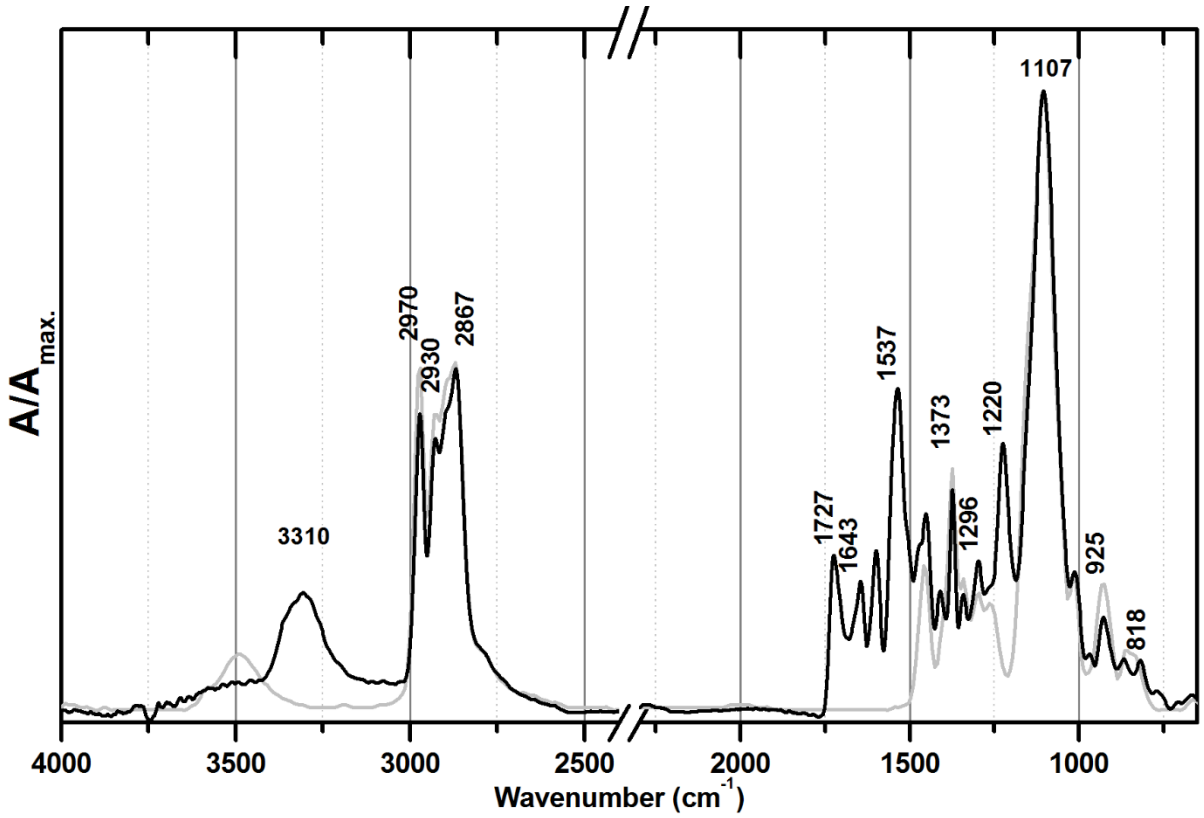


Figure IV.1 Infrared spectra of the model ether-based PUR slabstock foam (black) and poly(propylene glycol) (grey).

[166] The infrared spectrum of poly(propylene glycol), avg. Mw 3,000 was acquired from the Aldrich Condensed Phase Library database, Index 10385, CAS 25322-69-4.The spectra in this library are published in *The Aldrich Library of FT-IR Spectra*, vols. 1 and 2. Poly(propylene glycol) shows C–O–C stretching, C–H stretching, C–H deforming and the C–O–C stretching bands at c. 1110, c. 2869, c. 1454 and between 1150–1070 cm^{-1}, respectively (Suthanthiraraj *et al.*, 2009).

Table IV.1 Infrared assignment for the model ether-based PUR slabstock foam

Band (Wavenumber/cm^{-1})	**Assignment**	**Reference**
3743–3419 (w)	ν(N–H) free of H-bonds	(Dannoux *et al.*, 2005; Yilgör *et al.*, 2015)
3310 (m)	ν(N–H) H-bonded	(Dannoux *et al.*, 2005; Guignot *et al.*, 2001)
2970 (s)	$\nu_a(C–H_2)$	(Li *et al.*, 2012)
2930 (s)	$\nu_a(C–H_2)$	(Dannoux *et al.*, 2005)
2891 (s)	$\nu_s(C–H_2)$	(Li *et al.*, 2012)
2867 (s)	$\delta(C–H_3)\ \nu_s(C–H_2)$	(Li *et al.*, 2012)
1727 (m)	ν(C=O) urethane, free of H-bonds	(Priester *et al.*, 1990; Elwell *et al.*, 1996; Lan *et al.*, 2014; Yilgör *et al.*, 2015)
1712 (sld)	ν(C=O) urethane, loosely associated through H-bonds	(Priester *et al.*, 1990; Elwell *et al.*, 1996; Lan *et al.*, 2014; Yilgör *et al.*, 2015 and citations therein)
1643 (m)	ν(C=O) urea (strongly H-bonded, bidentate urea)	(Priester *et al.*, 1990; Elwell *et al.*, 1996; Lan *et al.*, 2014; Yilgör *et al.*, 2015)
1600 (m)	ν(C=C) benzene ring	(Dannoux *et al.*, 2005)
1537 (s)	ν(C–N) and δ(N–H)	(Dannoux *et al.*, 2005; Yilgör *et al.*, 2015)
1473, 1454 (m)	$\delta(C–H_2)$	(Dannoux *et al.*, 2005)
1373 (s), 1343	$\omega\ (C–H_2)$	(Guignot *et al.*, 2001)
1296 (m)	ν(C–N)	(Dannoux *et al.*, 2005)
1220 (s)	ν(C–N)	(Dannoux *et al.*, 2005)
1107 (vs)	$\nu(C–O–C)_{as}$ polyether-based polyol	(Guignot *et al.*, 2001)
868, 817, 769 (w)	ω (C–H) benzene ring	(Dannoux *et al.*, 2005)
756–676 (vw)	δ(C–H) benzene ring	(Dannoux *et al.*, 2005)

m – medium; s – strong; sld – shoulder; vs – very strong; vw – very weak; w - weak
δ - bending; ω - wagging; ν - stretching; a - anti-symmetric; s – symmetric

IV.2 Ester-based PUR slabstock foam

TDI-65 diisocyanate and polyester-based polyols mainly based on adipic acid-diethylene glycol polyester[167] (Fig. IV.2). The assignment of the main IR bands is shown in Table IV.2.

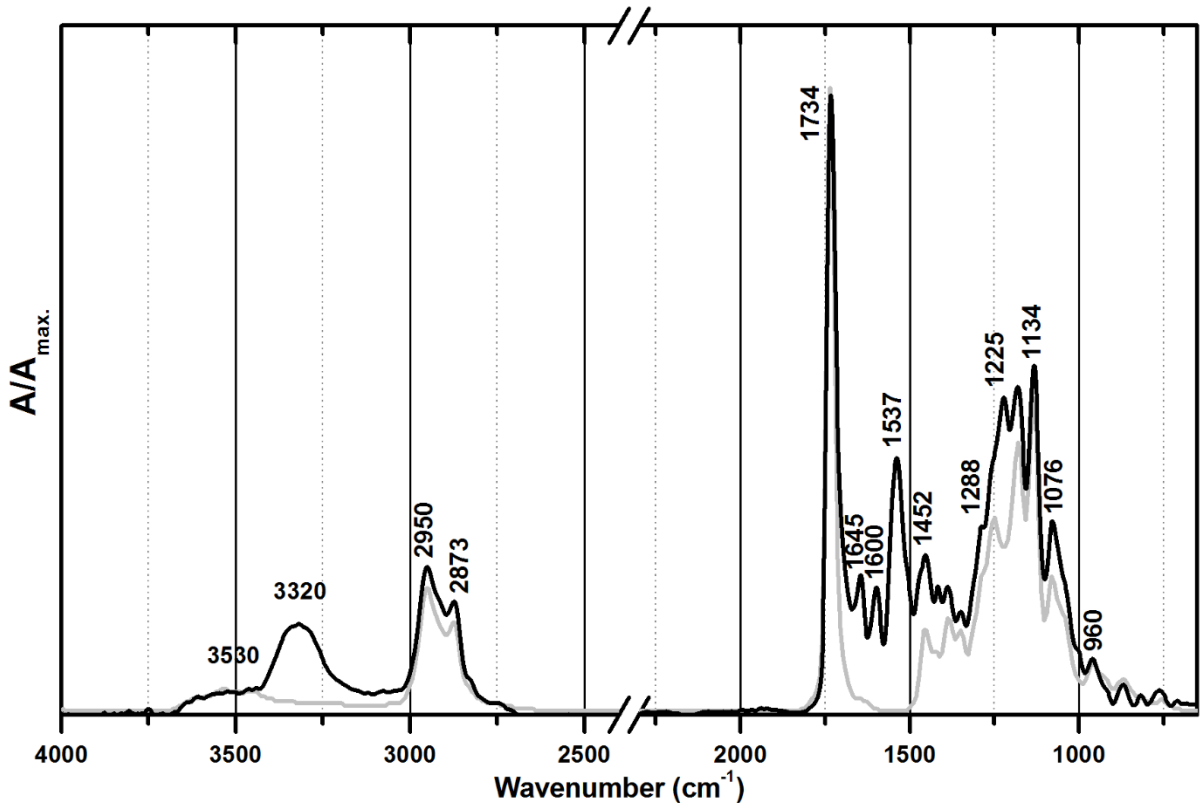


Figure IV.2 Infrared spectra of the model ester-based PUR slabstock foam (black) and adipic acid-diethylene glycol polyester (grey).

[167] The infrared spectrum of adipic acid-diethylene glycol polyester was acquired from the Coatings Technology Library database, Index 417. The spectra in this library are published in *An Infrared Spectroscopy Atlas for the Coatings Industry, Fourth Edition.* Adipic acid-diethylene glycol polyester shows IR bands at c. 2950 and c. 2870 cm^{-1} (C–H and C=O stretching vibrations, respectively), at 1734 cm^{-1} (C=O stretching) and a broad band between 3450–3600 cm^{-1} (O–H stretching end-groups) (Siriphannon & Monvisade: 2008).

Table IV.2 Infrared assignment for the model ester-based PUR slabstock foam

Band (Wavenumber/cm^{-1})	**Assignment**	**Reference**
3670–3425 (w)	ν(N–H) free of H-bonds	(Wilhelm & Gardette, 1997 and citations therein; Dannoux *et al*., 2005; Yilgör *et al*., 2015)
3320 (m)	ν(N–H) H-bonded	(Wilhelm & Gardette, 1997 and citations therein; Dannoux *et al*., 2005; Guignot *et al*., 2001)
2950 (m)	$\nu_a(C–H_2)$	(Wilhelm & Gardette, 1997 and citations therein; Li *et al*., 2012)
2873 (m)	$\nu_s(C–H_2)$	(Wilhelm & Gardette, 1997 and citations therein)
1734(vs)	ν(C=O) ester and urethane, free of H-bonds	(Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Lan *et al*., 2014; Yilgör *et al*., 2015)
1645 (m)	ν(C=O) urea (strongly H-bonded, bidentate urea)	(Priester *et al*., 1990; Elwell *et al*., 1996; Lan *et al*., 2014; Yilgör *et al*., 2015)
1600 (m)	ν(C=C) benzene ring	(Dannoux *et al*., 2005)
1537 (s)	ν(C–N) and δ(N–H)	(Dannoux *et al*., 2005; Yilgör *et al*., 2015)
1452 (m)	$\delta(C–H_2)$	(Dannoux *et al*., 2005)
1415 (m)	$\delta(C–H_2)$	(Wilhelm & Gardette, 1997)
1388 (m)	$\omega\ (C–H_2)$	(Guignot *et al*., 2001)
1350 (m)	$\omega\ (C–H_2)$	(Schoonover *et al*., 2001)
1288 (m)	ν(C–N)	(Dannoux *et al*., 2005)
1225 (s)	ν(C–N) and δ(N–H)	(Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998)
1180 (s)	ν(C–O–C) ester	(Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Schoonover *et al*., 2001)
1134 (s)	$\nu(O–CH_2)$	(Wilhelm & Gardette, 1997; Schoonover *et al*., 2001)
1076 (m)	ν(C–O–C) urethane	(Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Schoonover *et al*., 2001)
871, 818, 761 (vw)	ω (C–H) benzene ring	(Dannoux *et al*., 2005)
709 (vw)	δ(C–H) benzene ring	(Dannoux *et al*., 2005)

m – medium; s – strong; sld – shoulder; vs – very strong; vw – very weak; w - weak
δ - bending; ω - wagging; ν - stretching; a - anti-symmetric; s – symmetric

IV.3 Ether-based PUR cold-moulded foam

Blends of TDI/MDI diisocyanates and polyether-based polyols mainly based on poly(propylene glycol) and poly(ethylene glycol)[168] (Fig. IV.3). The assignment of the main IR bands is shown in Table IV.3.

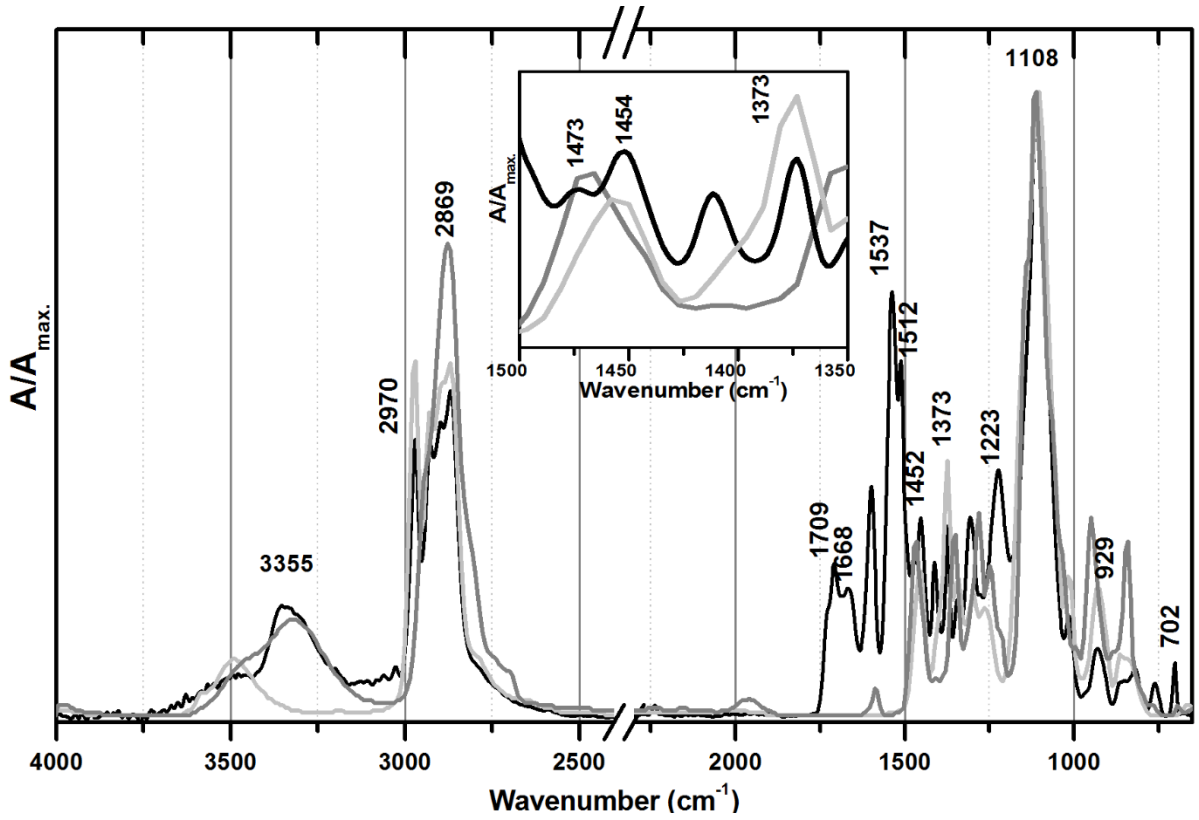


Figure IV.3 Infrared spectra of the model PUR cold-moulded foam (black), poly(propylene glycol) (light grey) and poly(ethylene glycol) (dark grey). Inset: detail of the CH_2 bending and wagging absorptions from 1500 to 1350 cm^{-1}.

[168] The infrared spectrum of poly(ethylene glycol), avg. Mw 3,400 was acquired from the Aldrich Condensed Phase Library database, Index 10391, CAS 25322-68-3.The spectra in this library are published in *The Aldrich Library of FT-IR Spectra*, vols. 1 and 2. Poly(ethylene glycol) main IR bands are detected at c. 1110 cm^{-1} (C–O–C stretching) and c. 2870 cm^{-1} (C–H stretching) and between 3300-3550 cm^{-1} (O–H stretching) (Kumar, 1990).

Table IV.3 Infrared assignment for the model PUR cold-moulded foam

Band (Wavenumber/cm^{-1})	**Assignment**	**Reference**
3740–3430 (w)	ν(N–H) free of H-bonds	(Dannoux *et al.*, 2005; Yilgör *et al.*, 2015)
3345 (m)	ν(N–H) H-bonded	(Dannoux *et al.*, 2005; Guignot *et al.*, 2001)
2970 (s)	$\nu_a(C–H_2)$	(Li *et al.*, 2012)
2930 (s)	$\nu_a(C–H_2)$	(Dannoux *et al.*, 2005;)
2897 (s)	$\nu_s(C–H_2)$	(Li *et al.*, 2012)
2869 (s)	$\delta(C–H_3)\ \nu_s(C–H_2)$	(Li *et al.*, 2012)
1709 (m)	ν(C=O) urethane, (loosely associated through H-bonds)	(Priester *et al.*, 1990; Elwell *et al.*, 1996; Lan *et al.*, 2014; Yilgör *et al.*, 2015 and citations therein)
1668 (m)	ν(C=O) urea (loosely associated through H-bonds, monodentate urea)	(Priester *et al.*, 1990; Elwell *et al.*, 1996; Lan *et al.*, 2014; Yilgör *et al.*, 2015)
1600 (m)	ν(C=C) benzene ring	(Dannoux *et al.*, 2005)
1537 (s), 1512 (s)	ν(C–N) and δ(N–H)	(Dannoux *et al.*, 2005; Yilgör *et al.*, 2015)
1473 (m), 1454 (m)	$\delta(C–H_2)$	(Dannoux *et al.*, 2005)
1373 (m), 1346 (m)	$\omega\ (C–H_2)$	(Guignot *et al.*, 2001)
1307 (m)	ν(C–N)	(Dannoux *et al.*, 2005)
1223 (m)	ν(C–N)	(Dannoux *et al.*, 2005)
1108 (vs)	$\nu(C–O–C)_{as}$ polyether-based polyol	(Guignot *et al.*, 2001)
858, 819 (vw)	ω(C–H) benzene ring	(Dannoux *et al.*, 2005)
759 (vw)	δ(C–H) benzene ring	(Dannoux *et al.*, 2005)

m – medium; s – strong; vs – very strong; vw – very weak; w - weak
δ - bending; ω - wagging; ν - stretching; a - anti-symmetric; s – symmetric

IV.4 Ester-based TPU film

MDI diisocyanate and polyester-based polyol possibly based on poly(1,4-butylene adipate)[169]. (Fig. IV.4). In addition, 1,4-butanediol (BD) could has been used as the chain extender since no urea bands are shown (contrary to polyurethanes chain extended by amine compounds). The assignment of the main IR bands is shown in Table IV.4.

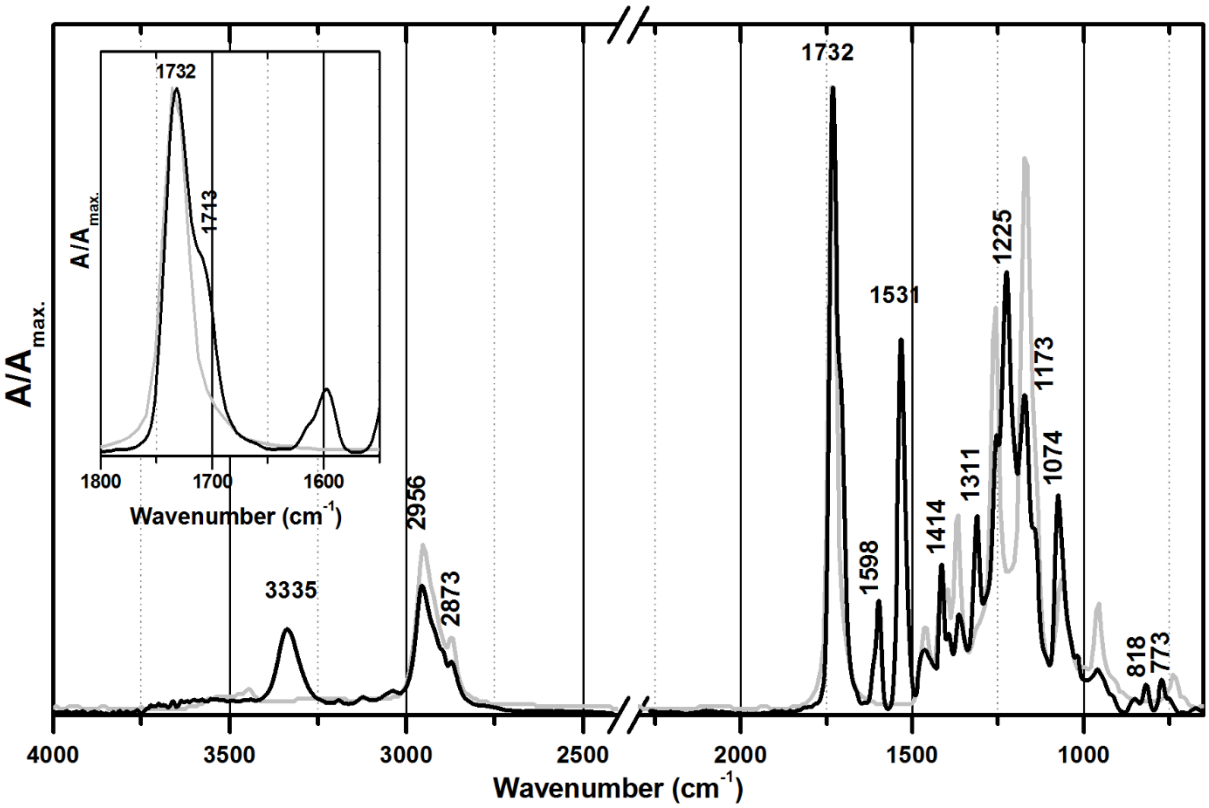


Figure IV.4 Infrared spectra of the model TPU film (black) and poly(1,4-butylene adipate) (grey). Inset: detail of the carbonyl stretching region from 1800 to 1600 cm^{-1}.

[169] The infrared spectrum of poly(1,4-butylene adipate) was acquired from the Aldrich Condensed Phase Library database, Index 10448, CAS 25103-87-1.The spectra in this library are published in *The Aldrich Library of FT-IR Spectra*, vols. 1 and 2. Poly(1,4-butylene adipate) shows characteristic IR bands at c. 1730 cm^{-1} (C=O stretching), c. 1260 and c. 1175 cm^{-1} (C–O–C stretching) and at c. 2955 and 2870 cm^{-1} (C–H stretching) (Yan *et al.*, 2008).

Table IV.4 Infrared assignment for the model ester-based TPU film

Band (Wavenumber/cm^{-1})	**Assignment**	**Reference**
3750–3415 (vw)	ν(N–H) free of H-bonds	(Wilhelm & Gardette, 1997 and citations therein; Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Dannoux *et al*., 2005; Yilgör *et al*., 2015)
3335 (m)	ν(N–H) H-bonded	(Wilhelm & Gardette, 1997 and citations therein; Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Dannoux *et al*., 2005; Guignot *et al*., 2001)
2956 (m)	$\nu_a(C–H_2)$	(Wilhelm & Gardette, 1997 and citations therein; Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Li *et al*., 2012)
2873 (m)	$\nu_s(C–H_2)$	(Wilhelm & Gardette, 1997 and citations therein)
1732 (vs)	ν(C=O) ester and urethane, free of H-bonds	(Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Lan *et al*., 2014; Yilgör *et al*., 2015)
1713 (sld)	ν(C=O) urethane, H-bonded	(Priester *et al*., 1990; Elwell *et al*., 1996; Lan *et al*., 2014; Yilgör *et al*., 2015)
1598 (m)	ν(C=C) benzene ring	(Dannoux *et al*., 2005)
1531 (s)	ν(C–N) and δ(N–H)	(Dannoux *et al*., 2005; Yilgör *et al*., 2015)
1464 (w)	$\delta(C–H_2)$	(Dannoux *et al*., 2005)
1414 (m)	$\delta(C–H_2)$	(Wilhelm & Gardette, 1997)
1363 (w)	$\omega\ (C–H_2)$	(Guignot *et al*., 2001)
1311 (s)	ν(C–N), δ(N-H) and δ(C–H)	(Dannoux *et al*., 2005; Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Schoonover *et al*., 2001)
1255 (sld)	ν (C–O–C) and $\omega(C–H_2)$	(Schoonover *et al*., 2001)
1225 (s)	ν(C–N) and δ(N–H)	(Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998)
1173 (s)	ν(C–O–C) ester	(Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Schoonover *et al*., 2001)
1074 (s)	ν(C–O–C) urethane	(Srichatrapimuk & Cooper, 1978 *apud* Marsh & Schoonover, 1998; Schoonover *et al*., 2001)
818 (vw)	ω (C–H) benzene ring	(Dannoux *et al*., 2005)
773 (vw)	δ(C–H) benzene ring	(Dannoux *et al*., 2005)

m – medium; s – strong; sld – shoulder; vs – very strong; vw – very weak; w - weak
δ - bending; ω - wagging; ν - stretching; a - anti-symmetric; s – symmetric

Appendix V – Characterisation of case studies

V.1. Infrared and Raman characterisation of PUR foams from selected case studies from the MUDE collection

Identifying the chemical composition of a plastic object and understanding its physical and chemical stability are one of the most important tasks in plastics conservation (van Oosten & Learner, 2012). To this end, several analytical methods have been applied. Infrared spectroscopy is the most widely used technique to identify polymer types (Shashoua, 2009; van Oosten & Learner, 2012). As stated by Picollo *et al*., 'In fact, FT-IR analysis in the mid-infrared (mid-IR) spectral region gives researchers considerable ability to distinguish and identify polymers, and meets requirements such as micro-destructiveness (and, in certain circumstances, nondestructiveness), cost effectiveness, and the availability of a wide range of commercial instrumentation' (Picollo *et al*., 2014: 390). Accordingly, several conservation studies using IR spectroscopy and focused on the study of plastics in art and design can be found in the literature (Lazzari *et al*., 2011; Toja *et al*., 2012; Picollo *et al*., 2014; Saviello *et al*., 2015). In which concerns Raman spectroscopy, although less attention has been given to this analytical approach, in recent years it has started to gain an increased interest in the field of plastics conservation. According to Vašková, 'Doubtless advantages as non-destructiveness, contactless measurements, rapidity or no demand for sample preparation makes Raman spectroscopy attractive, convenient and effective' (Vašková, 2011: 1205). Regarding its use in the characterisation of polymers, Raman spectroscopy has been able to provide information about polymer structures and spatial arrangement of molecules. Thus, both Raman and infrared spectroscopies are regarded as complementary techniques, which more and more have been advantageously used for polymerisation and ageing studies of synthetic polymers. As supported by the literature, 'Raman spectra contain much information in the lower frequency range where there is little absorbance in infrared spectra' (Shashoua, 2009: 138), and 'Infrared spectroscopy has more intensive signal for small polar molecules and single bonded chemical compounds like C–C, C–O, C–H etc' (Vašková, 2011: 1206). On the other hand, several drawbacks can also be attributed to Raman spectroscopy, namely heating, degradation and fluorescence (Everall, 2002). Samples can suffer laser-induced heating due to high intensity at the laser focus (especially coloured samples); dark samples are easily damaged (burned) due to laser-induced degradation; and if the laser light is absorbed by the sample, the probability of exciting fluorescence is high (especially when using short wavelength lasers). This can change the signal-to-noise ratio (S/N) of the Raman spectrum in a high extent, making impossible to obtain a spectrum with good spectral resolution. For the

characterisation of hydrogen-bonding interactions, the fluorescence effect is highly depreciated. As these weak interactions cause small changes in a Raman spectrum, high resolutions are required in order to detect them. In this research, yellowed PUR foams were confirmed as more prone to fluorescence than less yellowed samples, and consequently, their analysis by Raman spectroscopy showed increased difficulties.

In the light of these facts, this appendix intends to highlight both techniques as powerful tools but mostly as complementary approaches for both material identification and condition assessment of PUR foams.

To stress their usefulness in the distinction of PUR condition grades, the spectrum of each case study spectrum is compared with the respective unaged model spectrum. As shown, when analysing whitish or slight yellowed samples (see Chapter 3), Raman spectroscopy proved to be efficient in the acquisition of spectra with good resolution. Conversely, high yellowed samples (orange and brown) – mostly found in poor and unacceptable conditions – and black foams were not possible to analyse because of fluorescence effect or laser-induced degradation (burns). In addition to the condition assessment of PUR foams, Raman spectroscopy was also sensitive to distinguish processing methods within ether-based PUR foams. As examples, Raman spectroscopy has been able to distinguish slabstock and moulded foams, and to identify the addition of additives such as styrene-acrylonitrile copolymer (SAN) in PUR formulation. The results from infrared spectroscopy are discussed in detail in Chapter 3.

V.1.1 Ether-based PUR slabstock foams from selected case studies

Classified as fair condition

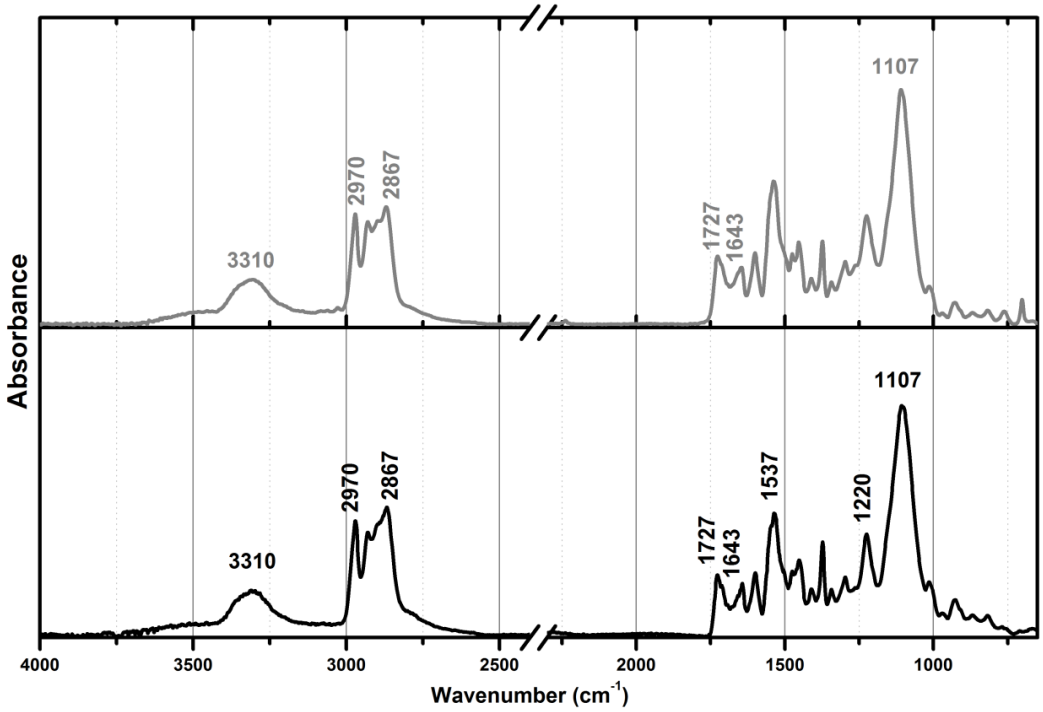


Figure V.1 Infrared spectra of unaged ether-based PUR foam model (black) and *Blue Bench* foam (grey) from 4000 to 650 cm^{-1}.

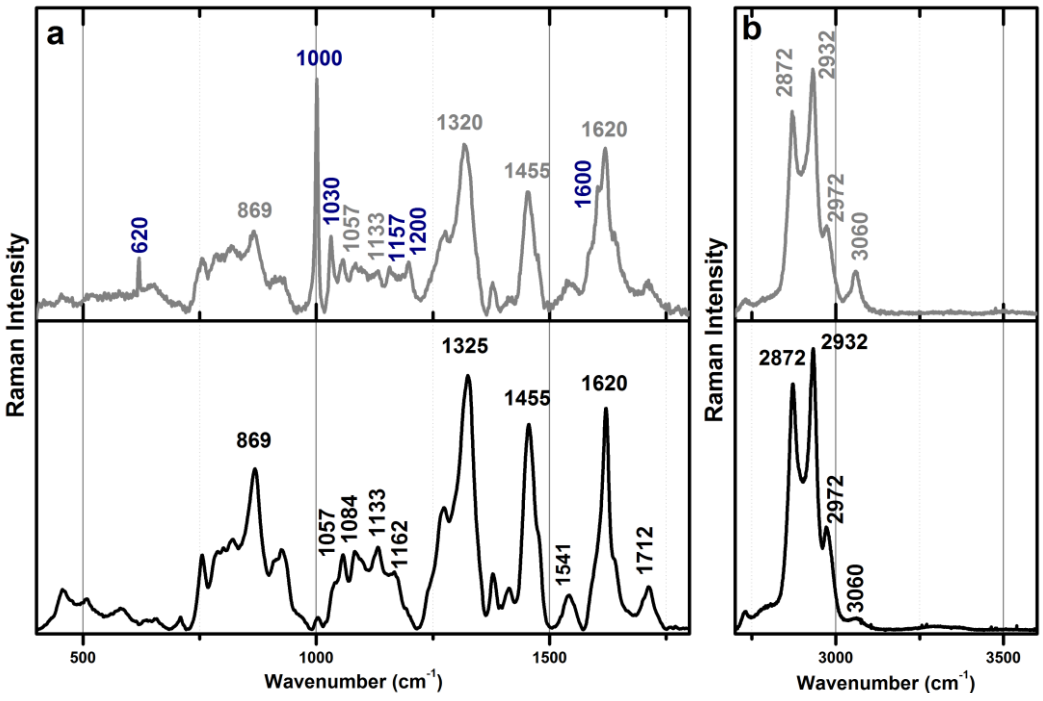


Figure V.2 Raman spectra of unaged ether-based PUR foam model (black) and *Blue Bench* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b). Wavenumbers marked in blue are assigned to styrene-acrylonitrile copolymer (SAN), added to the PUR foam formulation of *Blue Bench*.

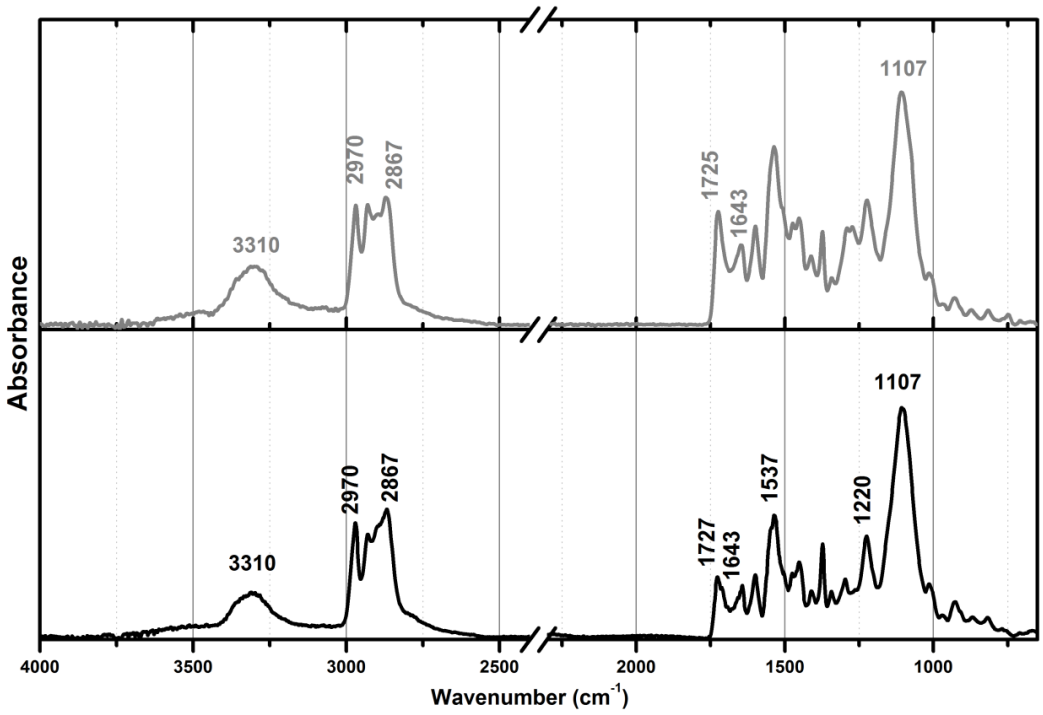


Figure V.3 Infrared spectra of unaged ether-based PUR foam model (black) and *Superonda* foam (grey) from 4000 to 650 cm^{-1}.

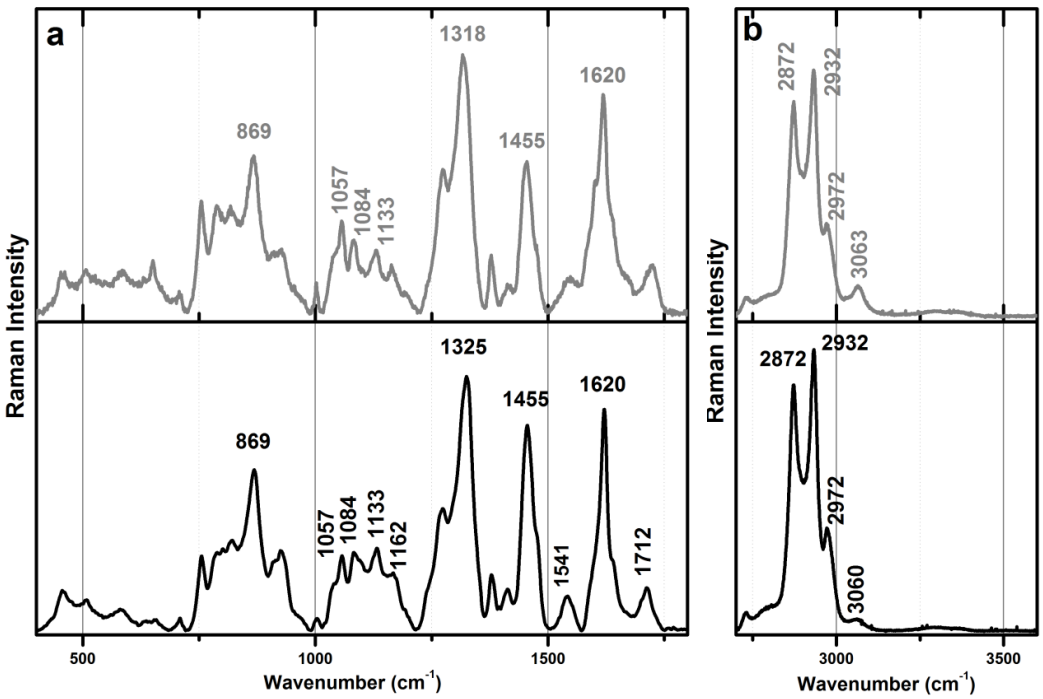


Figure V.4 Raman spectra of unaged ether-based PUR foam model (black) and *Superonda* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

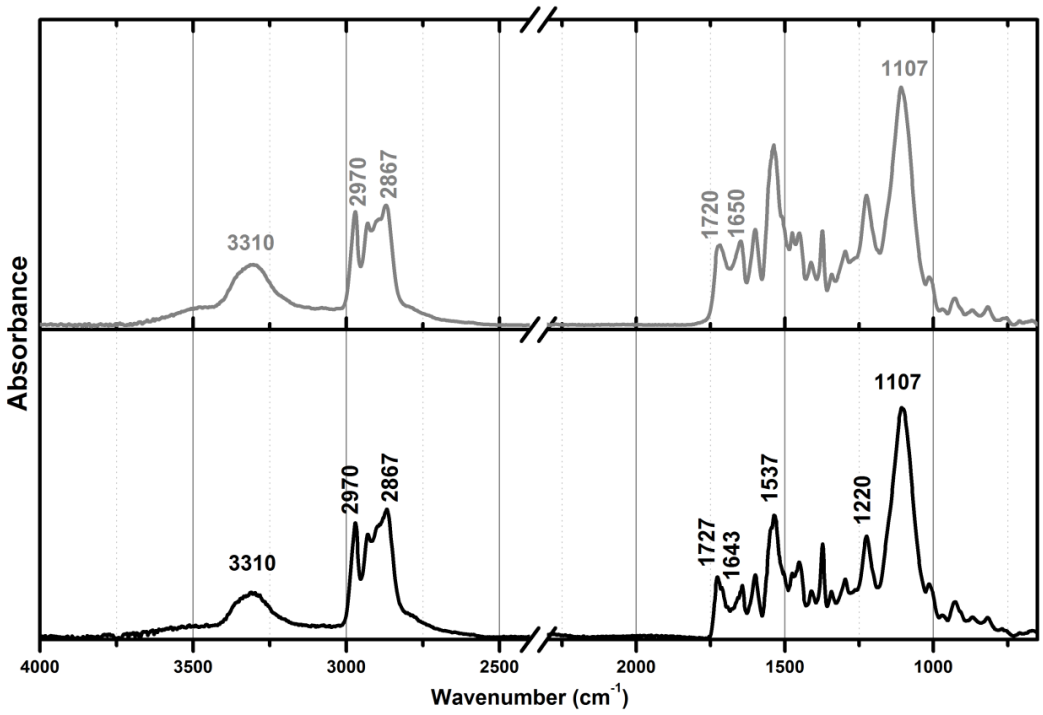


Figure V.5 Infrared spectra of unaged ether-based PUR foam model (black) and *Bocca* foam (grey) from 4000 to 650 cm^{-1}.

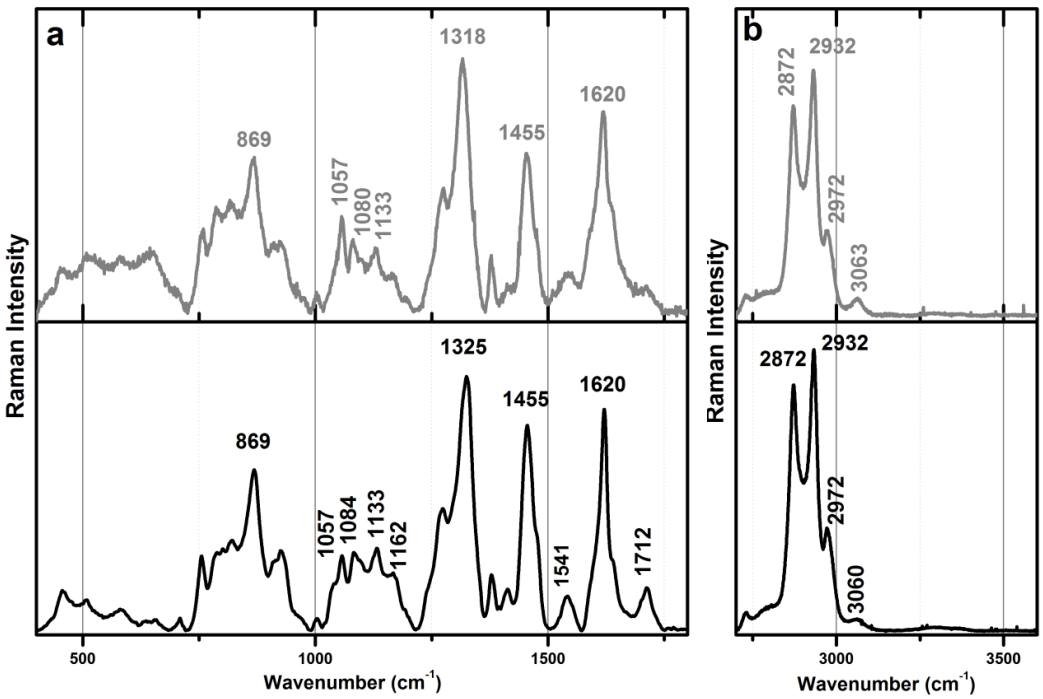


Figure V.6 Raman spectra of unaged ether-based PUR foam model (black) and *Bocca* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

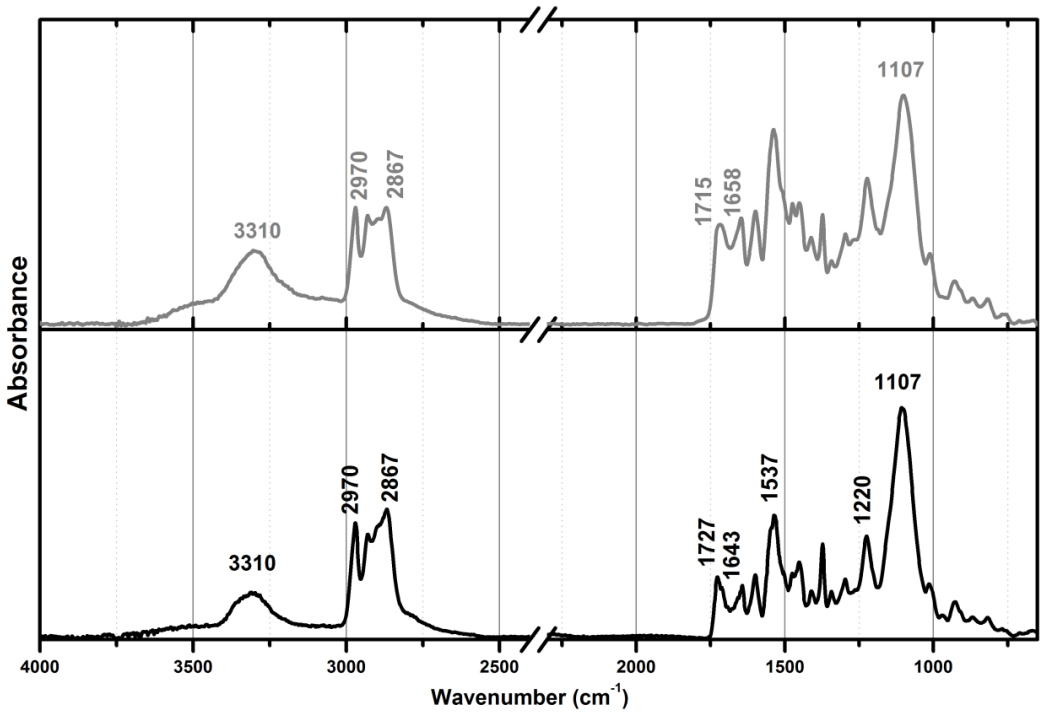


Figure V.7 Infrared spectra of unaged ether-based PUR foam model (black) and *Djinn* foam (grey) from 4000 to 650 cm^{-1}.

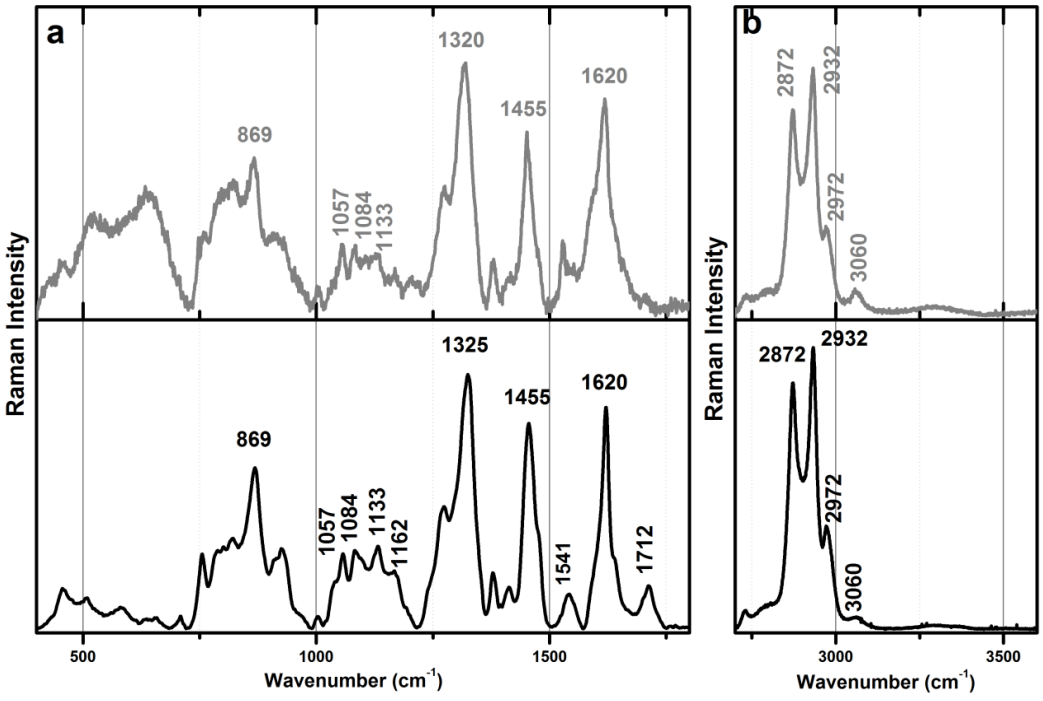


Figure V.8 Raman spectra of unaged ether-based PUR foam model (black) and *Djinn* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

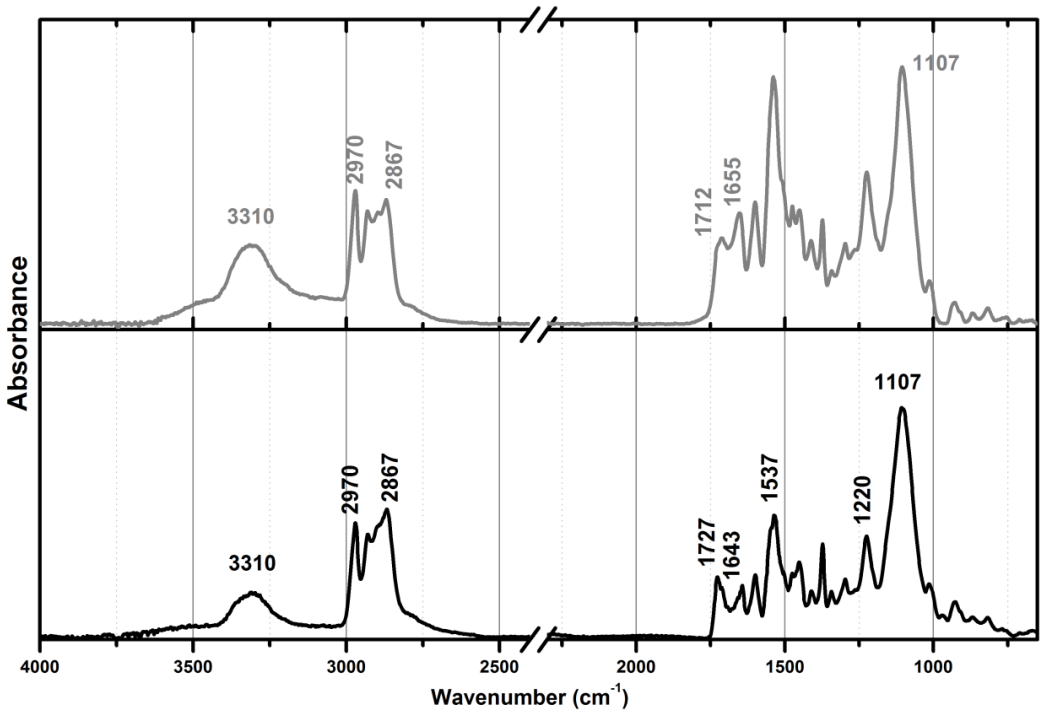


Figure V.9 Infrared spectra of unaged ether-based PUR foam model (black) and *Amphys* foam (grey) from 4000 to 650 cm^{-1}.

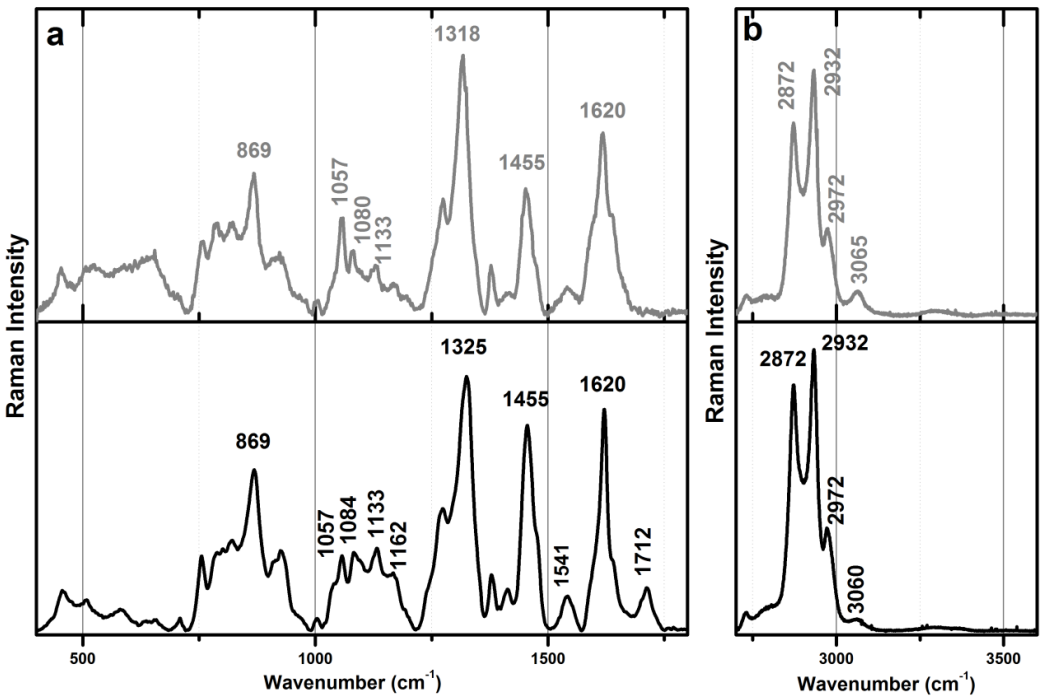


Figure V.10 Raman spectra of unaged ether-based PUR foam model (black) and *Amphys* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

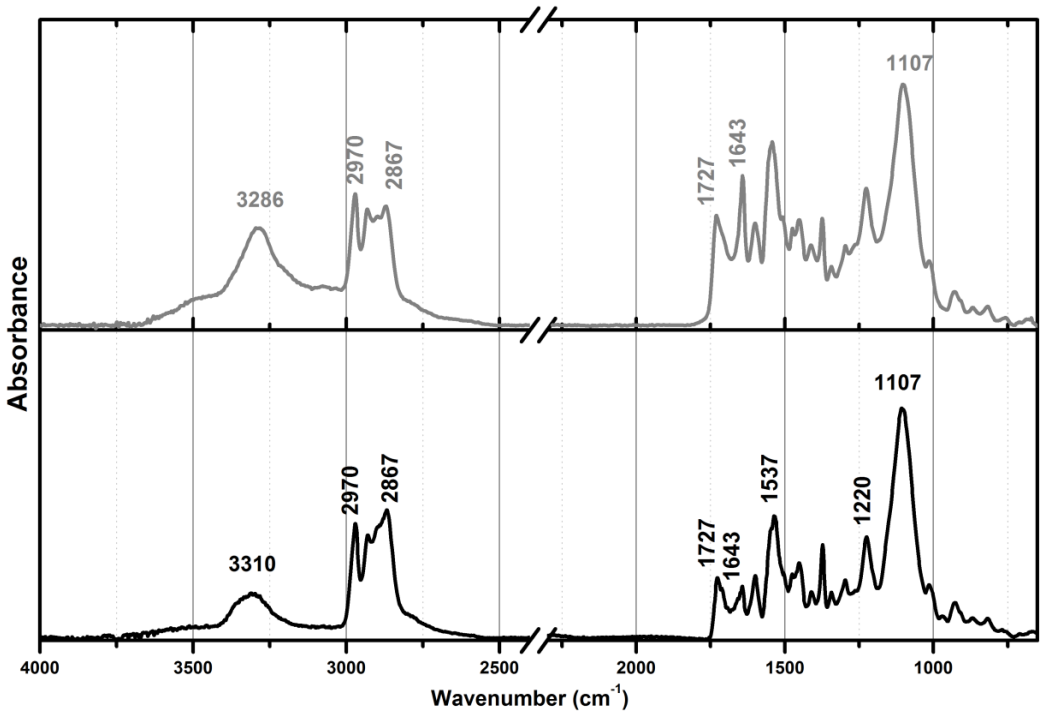


Figure V.11 Infrared spectra of unaged ether-based PUR foam model (black) and *Safari* yellow foam (grey) from 4000 to 650 cm^{-1}.

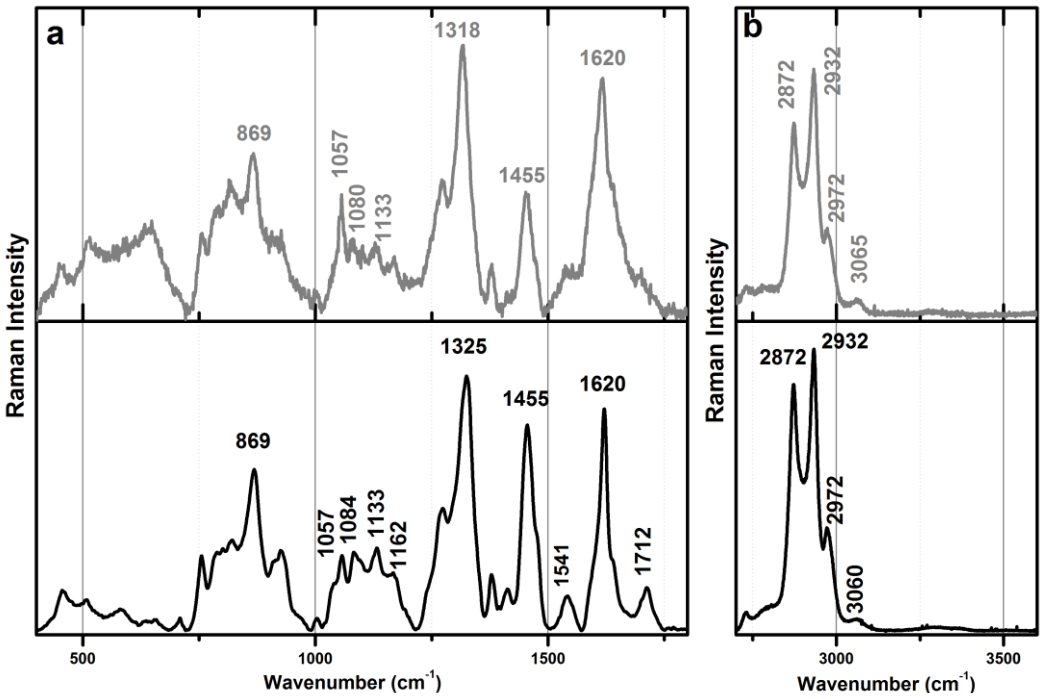


Figure V.12 Raman spectra of unaged ether-based PUR foam model (black) and *Safari* yellow foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

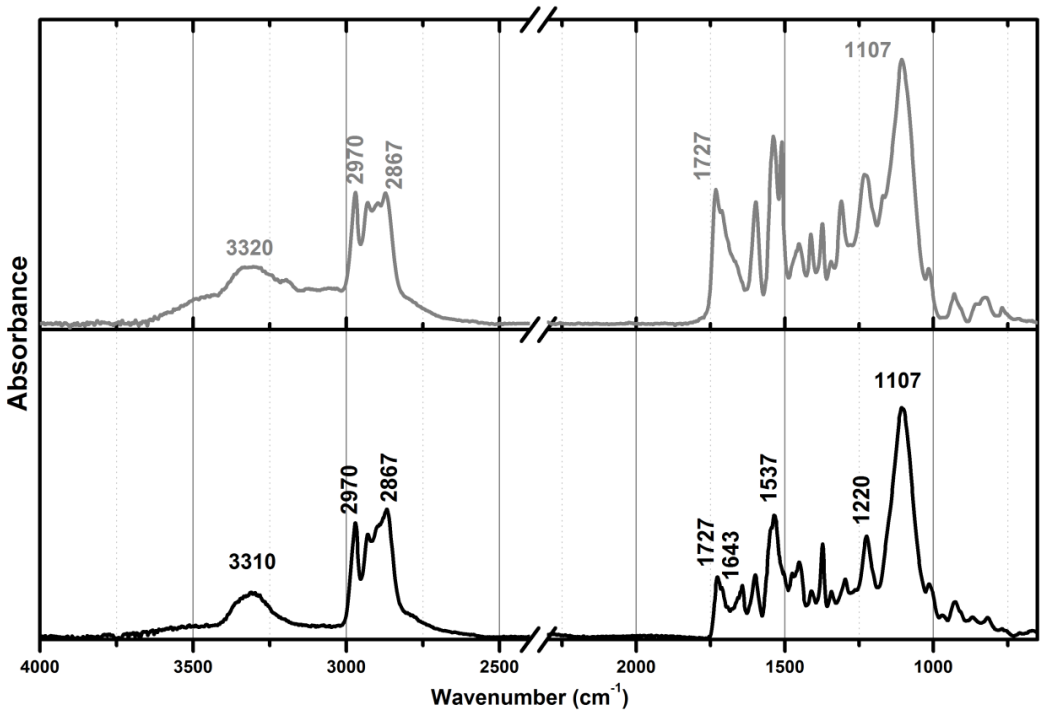


Figure V.13 Infrared spectra of unaged ether-based PUR foam model (black) and *Safari* orange foam (grey) from 4000 to 650 cm^{-1}.

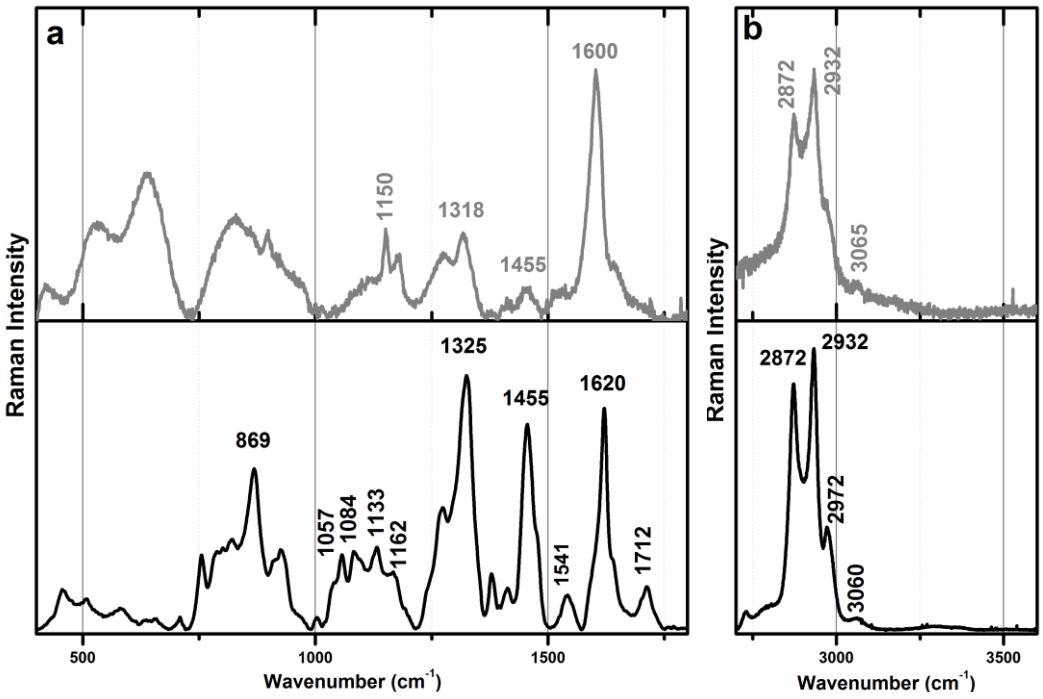


Figure V.14 Raman spectra of unaged ether-based PUR foam model (black) and *Safari* orange foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b).

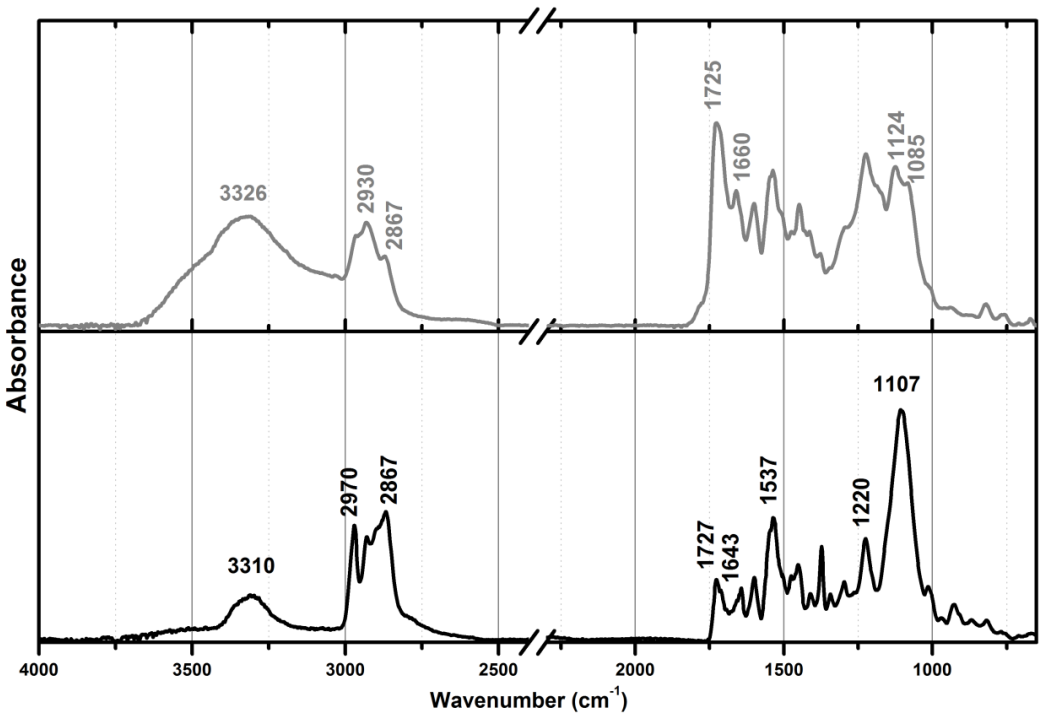


Figure V.15 Infrared spectra of unaged ether-based PUR foam model (black) and *Safari* orange foam (grey) from 4000 to 650 cm^{-1}.

It was not possible to collect any Raman spectrum from the brownish colour foam from *Safari* due to increased fluorescence effect.

V.1.2 Ether-based PUR cold-moulded foams from selected case studies

Classified as fair condition

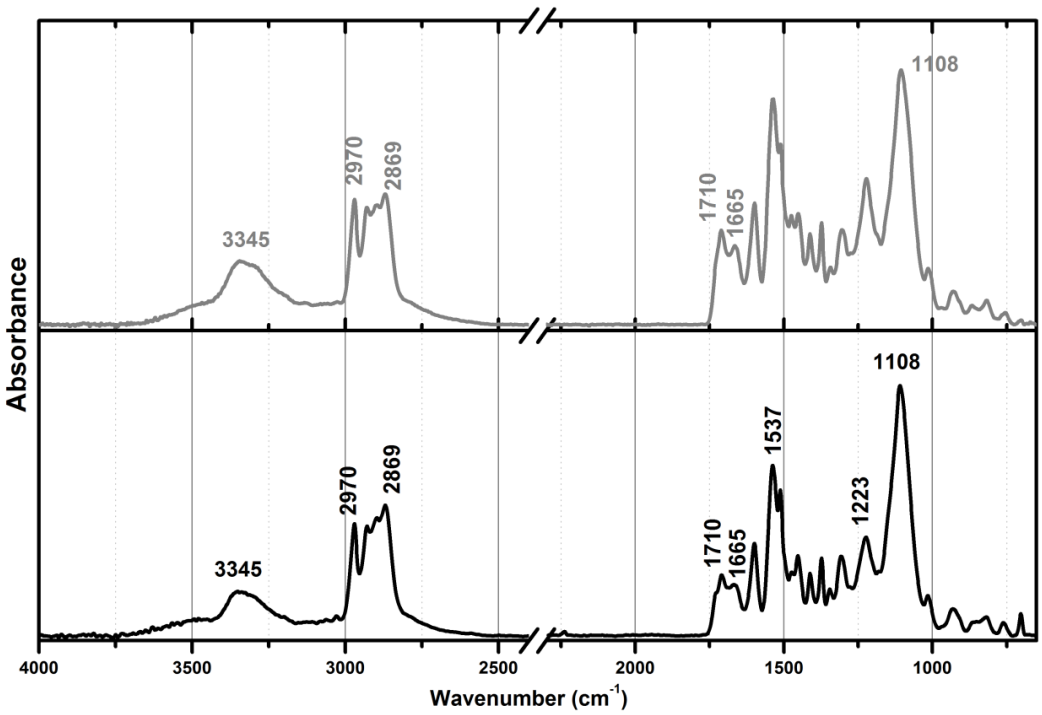


Figure V.16 Infrared spectra of unaged ether-based PUR foam model (black) and *Cactus* foam (grey) from 4000 to 650 cm^{-1}.

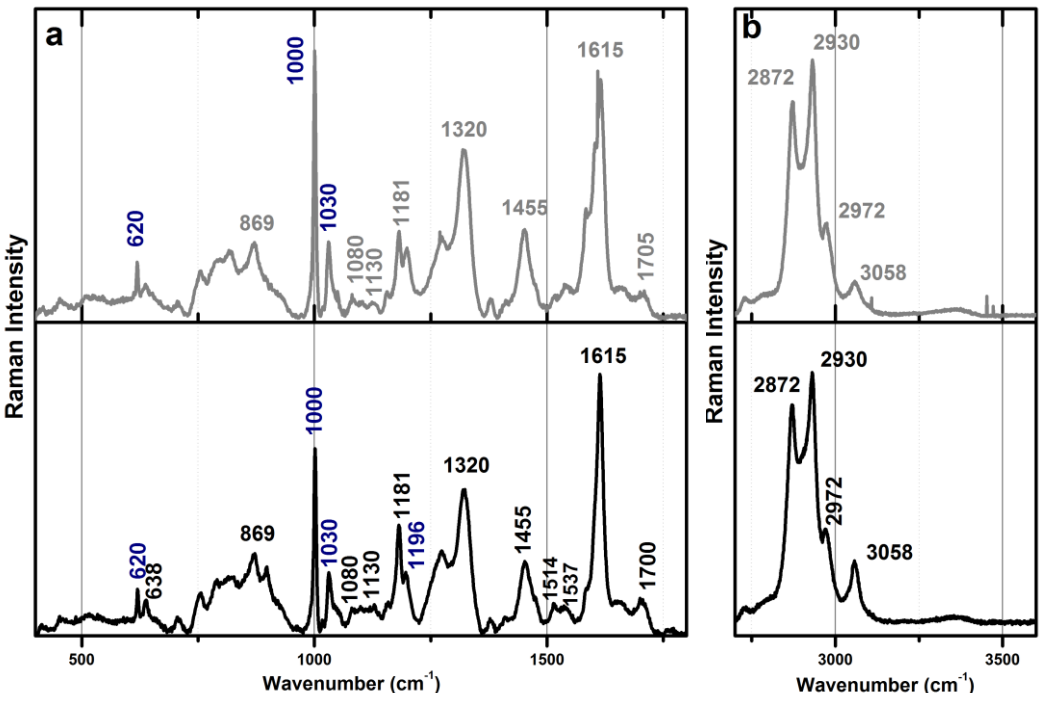


Figure V.17 Raman spectra of unaged ether-based PUR foam model (black) and *Cactus* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b). Wavenumbers marked in blue are assigned to styrene-acrylonitrile copolymer (SAN), additive of PUR foam formulation.

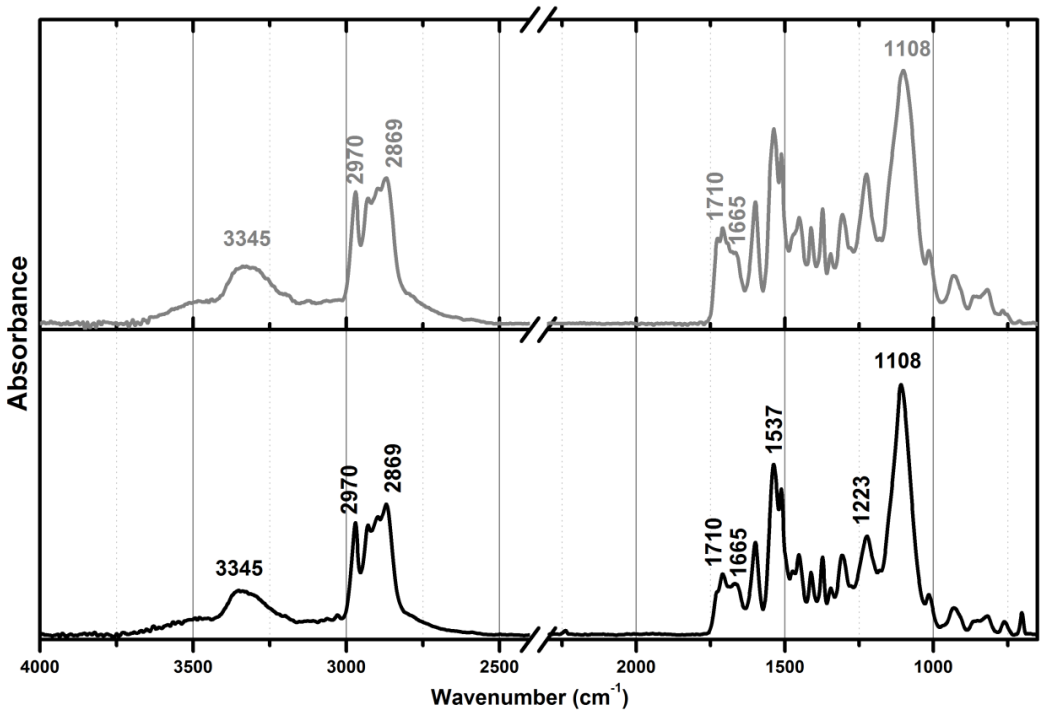


Figure V.18 Infrared spectra of unaged ether-based PUR foam model (black) and *Egg* foam (grey) from 4000 to 650 cm^{-1}.

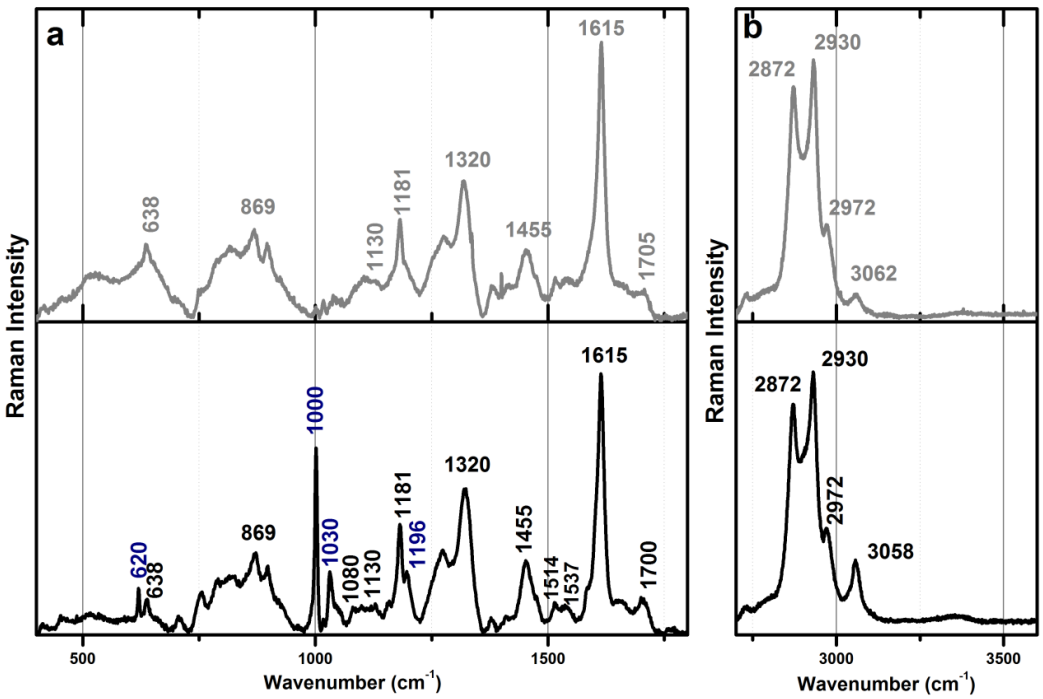


Figure V.19 Raman spectra of unaged ether-based PUR foam model (black) and *Egg* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b). Wavenumbers marked in blue are assigned to styrene-acrylonitrile copolymer (SAN), additive of the unaged PUR foam formulation.

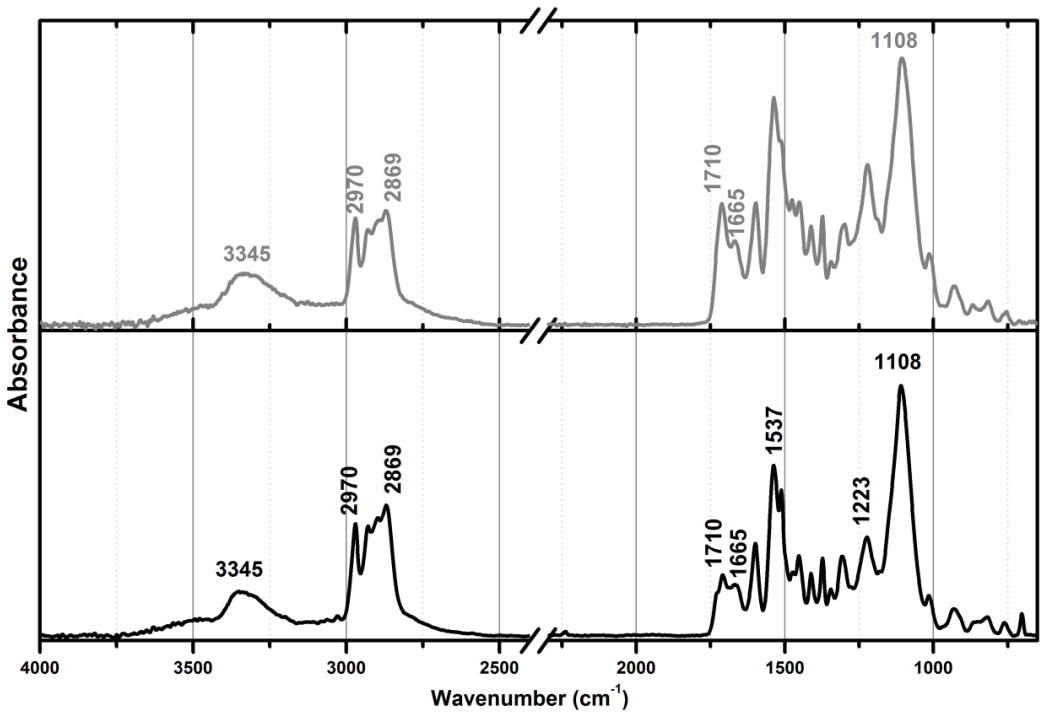


Figure V.20 Infrared spectra of unaged ether-based PUR foam model (black) and *Pratone* foam (grey) from 4000 to 650 cm^{-1}.

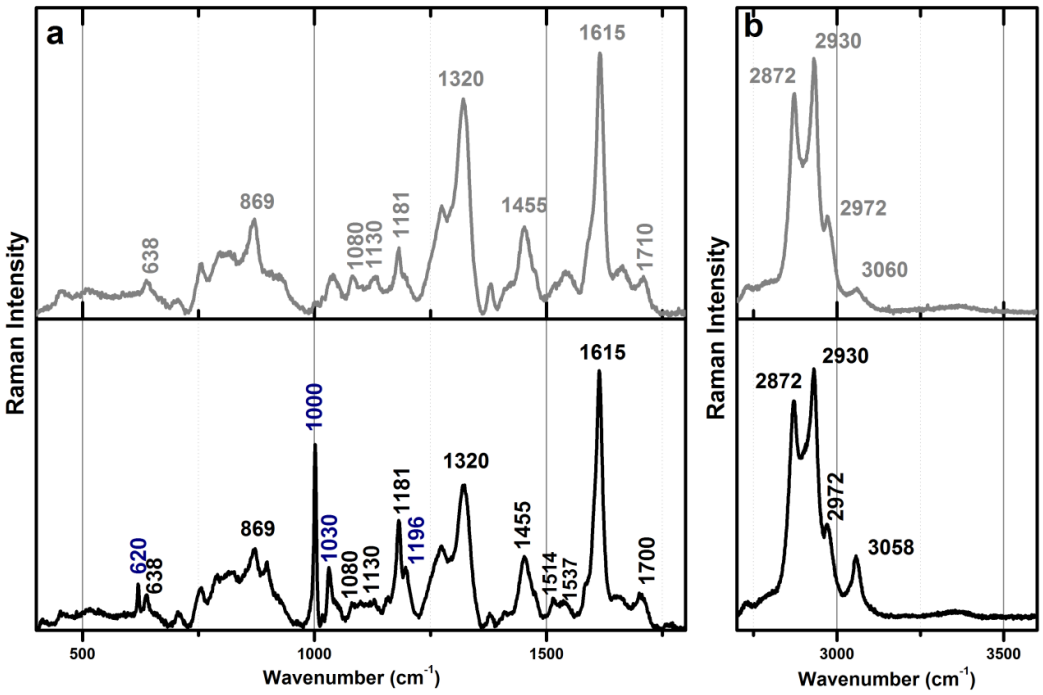


Figure V.21 Raman spectra of unaged ether-based PUR foam model (black) and *Pratone* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b). Wavenumbers marked in blue are assigned to styrene-acrylonitrile copolymer (SAN), additive of the unaged PUR foam formulation.

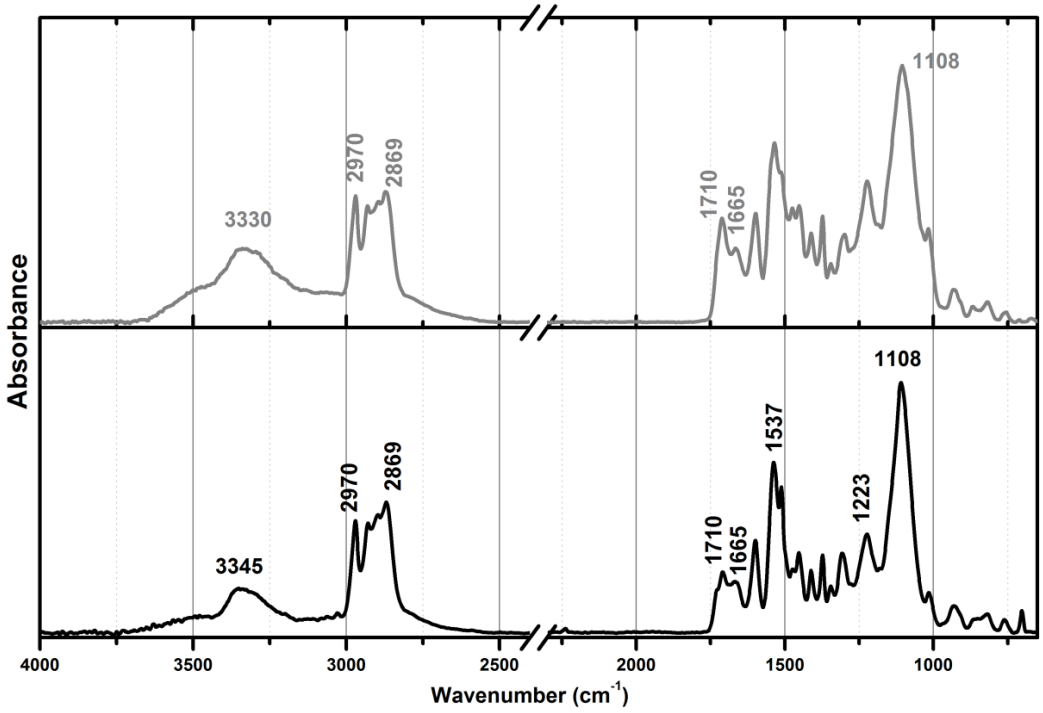


Figure V.22 Infrared spectra of unaged ether-based PUR foam model (black) and *Capitello* foam (grey) from 4000 to 650 cm^{-1}.

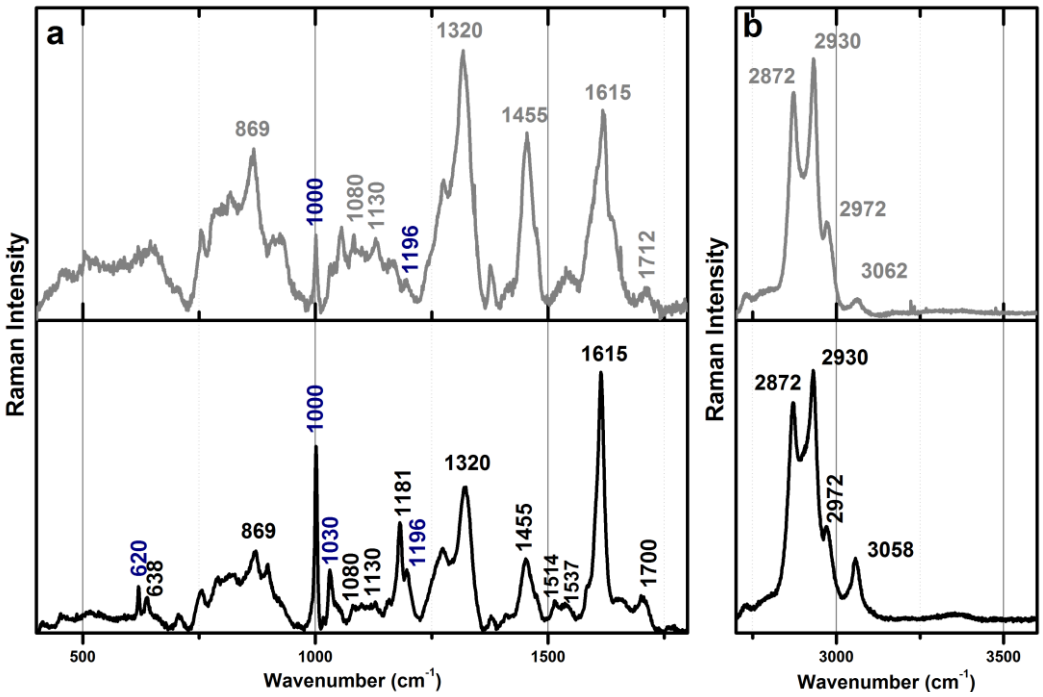


Figure V.23 Raman spectra of unaged ether-based PUR foam model (black) and *Capitello* foam (grey) from 400 to 1800 cm^{-1} (a) and from 2700 to 3600 cm^{-1} (b). Wavenumbers marked in blue are assigned to styrene-acrylonitrile copolymer (SAN), additive of the unaged PUR foam formulation.

V.2. Additional information on some case studies from the MUDE collection

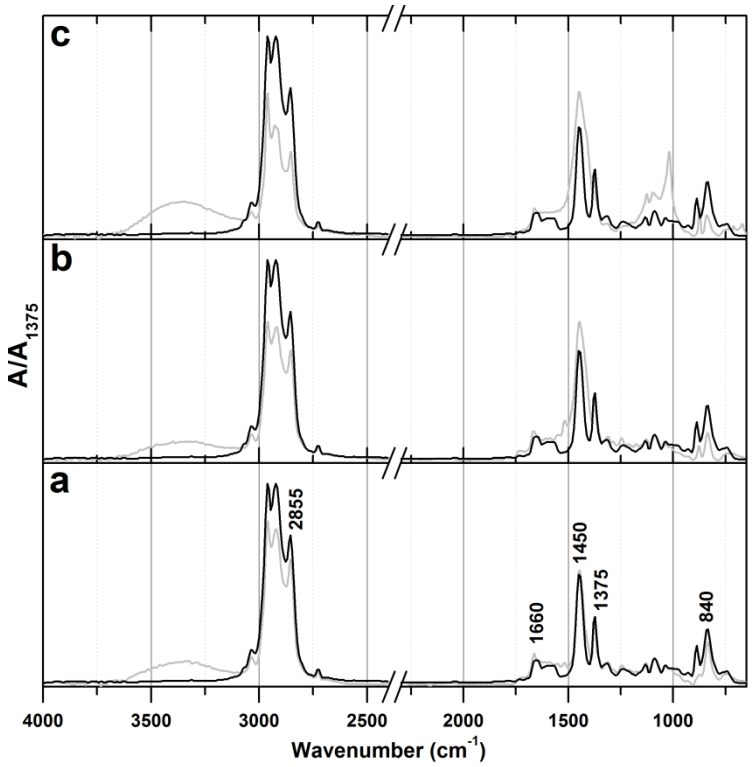


Figure V.24 Infrared spectra of poly(isoprene)[170], 1,4-cis (black) and the thick paint layers (grey) coating the foams from *Cactus* (a), *Pratone* (b) and *Capitello* (c).

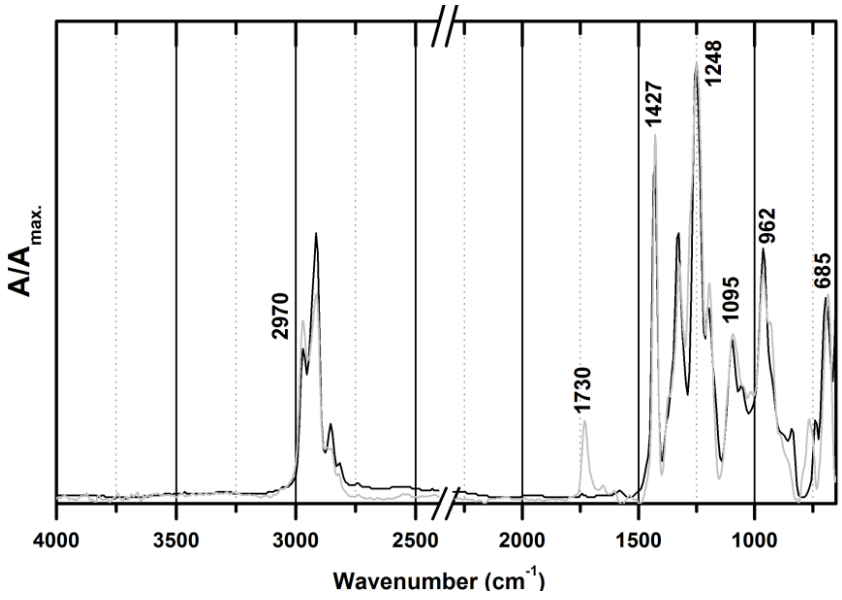


Figure V.25 Infrared spectra of poly(vinyl chloride)[171] (black) and the integral skin (grey) of the *Egg* foam.

[170] The infrared spectrum of poly(isoprene), 1,4-cis was obtained from the Hummel Polymer Additives Library database, Index 622, manufacturer H. Willersinn (BASF). The spectra of this library were compiled by Dr. Dieter O. Hummel at the Institut fur Physikalishche Chemie der Universitat Koln. Poly(isoprene), 1,4-cis shows infrared bands at c. 2855 cm^{-1} (C–H_2 stretching), 1660 cm^{-1} (C=C stretching), 1450 cm^{-1} (C–H_2 deformation) and 840 cm^{-1} (C–H wagging) (Adam et al., 1991).

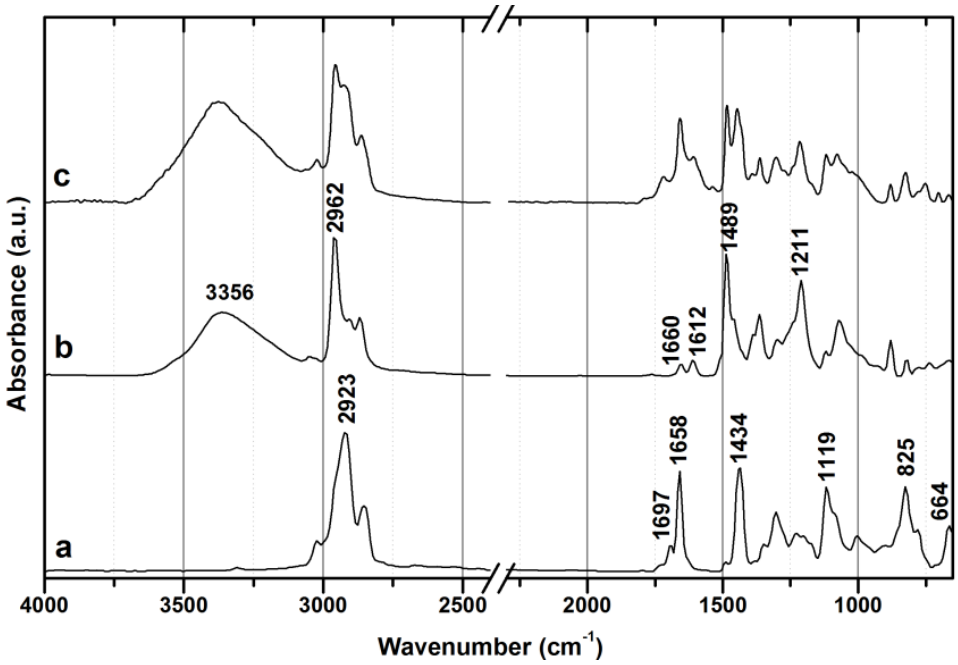


Figure V.26 Infrared spectra of polychloroprene[172] (a), phenolic resin[173] (b) and *Cactus* intermediate layer (c).

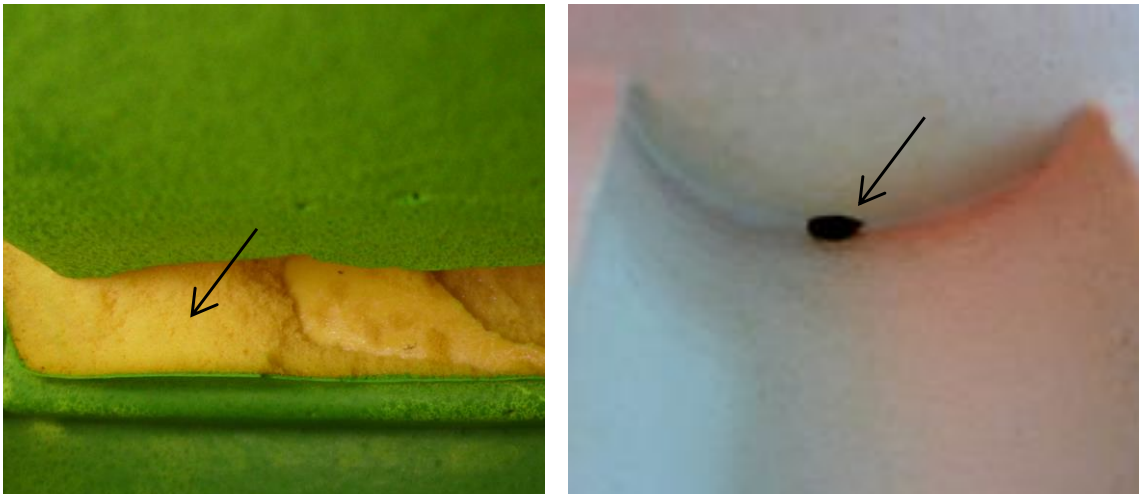


Figure V.27 Foam sampling areas for *Pratone* (left) and *Capitello* (right), as indicated by the arrows.

[171] The infrared spectrum of poly(vinyl chloride) was obtained from the Aldrich Condensed Phase Library database, Index 10361, CAS 9002-86-2.The spectra in this library are published in *The Aldrich Library of FT-IR Spectra*, vols. 1 and 2. Poly(vinyl chloride) shows several bands between 2800–3000 cm^{-1} (C–H stretching), at 1427 cm^{-1} (C–H deformation) and between 670–710 cm^{-1} (C–Cl stretching) (Tabb & Koenig, 1975).

[172] The infrared spectrum of poly(chloroprene) was obtained from the Hummel Polymer Additives Library database, Index 177, manufacturer Bayer Baypren 311. The spectra of this library were compiled by Dr. Dieter O. Hummel at the Institut fur Physikalishche Chemie der Universitat Koln. Poly(chloroprene) shows IR absorptions between 3100–2800 cm^{-1} (C–H stretching), at c. 1660 cm^{-1} (C=C stretching), 825 cm^{-1} (=C–H out-of-plane bending) and 660 cm^{-1} (C–Cl stretching) (Tabb *et al.*, 1975).

[173] The infrared spectrum of UCAR phenolic CK-1640 was obtained from the Coatings Technology Library database, Index 383. The spectra in this library are published in *An Infrared Spectroscopy Atlas for the Coatings Industry, Fourth Edition.* Phenolic resins show a broad band between 3100–3600 (O–H stretching), several bands between 3000–2800 cm^{-1} (C–H stretching) and characteristic bands at c. 1200 cm^{-1} (Ar–O stretching) and between 770–740 cm^{-1} (Ar–H out-of-plane bending) (Carotenuto & Nicolais, 1999).

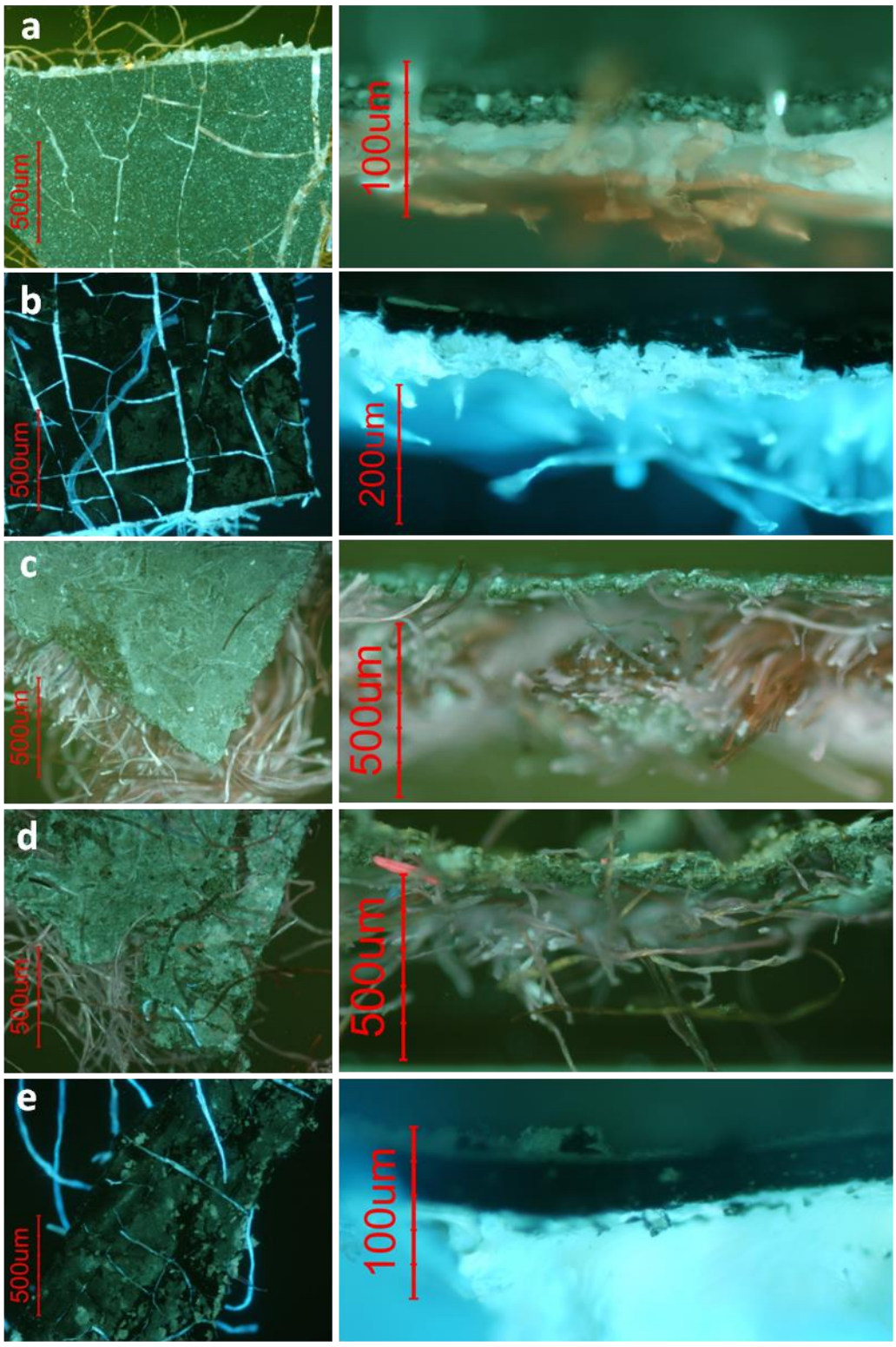


Figure V.28 Microscopy images of TPU coatings collected from the historical fashion garments showing different condition grades under blue-violet light. Surface (left) and cross section (right). Fair condition grade: brown dress (a). Poor condition grade: less degraded areas from the blue long jacket (b) and the blue dress (c). Unacceptable condition grade: more degraded areas from the blue dress (d) and blue long jacket (e).

Appendix VI – Ageing Studies

VI.1 Unaged model of ether-based PUR foam

VI.1.1 Weight variations

Weight measurements for the different exposure times are presented in Table VI.1. The values obtained are the result of three independent measurements.

Table VI.1 Weight variations (g) for the unaged ether-based PUR foam samples during the dark ageing experiment

Storage Condition	1 month		3 months		6 months		9 months		12 months	
	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)
Open-Air	-0.00236	-0.31051	0.00338	0.36901	0.00116	0.13181	0.00332	0.37635	0.00084	0.09798
Enclosed	-0.00310	-0.34781	0.00373	0.44657	0.00124	0.14518	0.00308	0.39091	0.00129	0.16346
Cool-enclosed	-0.00096	-0.10593	0.00548	0.67931	-0.00062	-0.08487	-0.00142	-0.16525	-0.00055	-0.07175
Anoxic	-0.00221	-0.29042	0.00349	0.47427	-0.00133	-0.15295	-0.00167	-0.21709	-0.00054	-0.06809

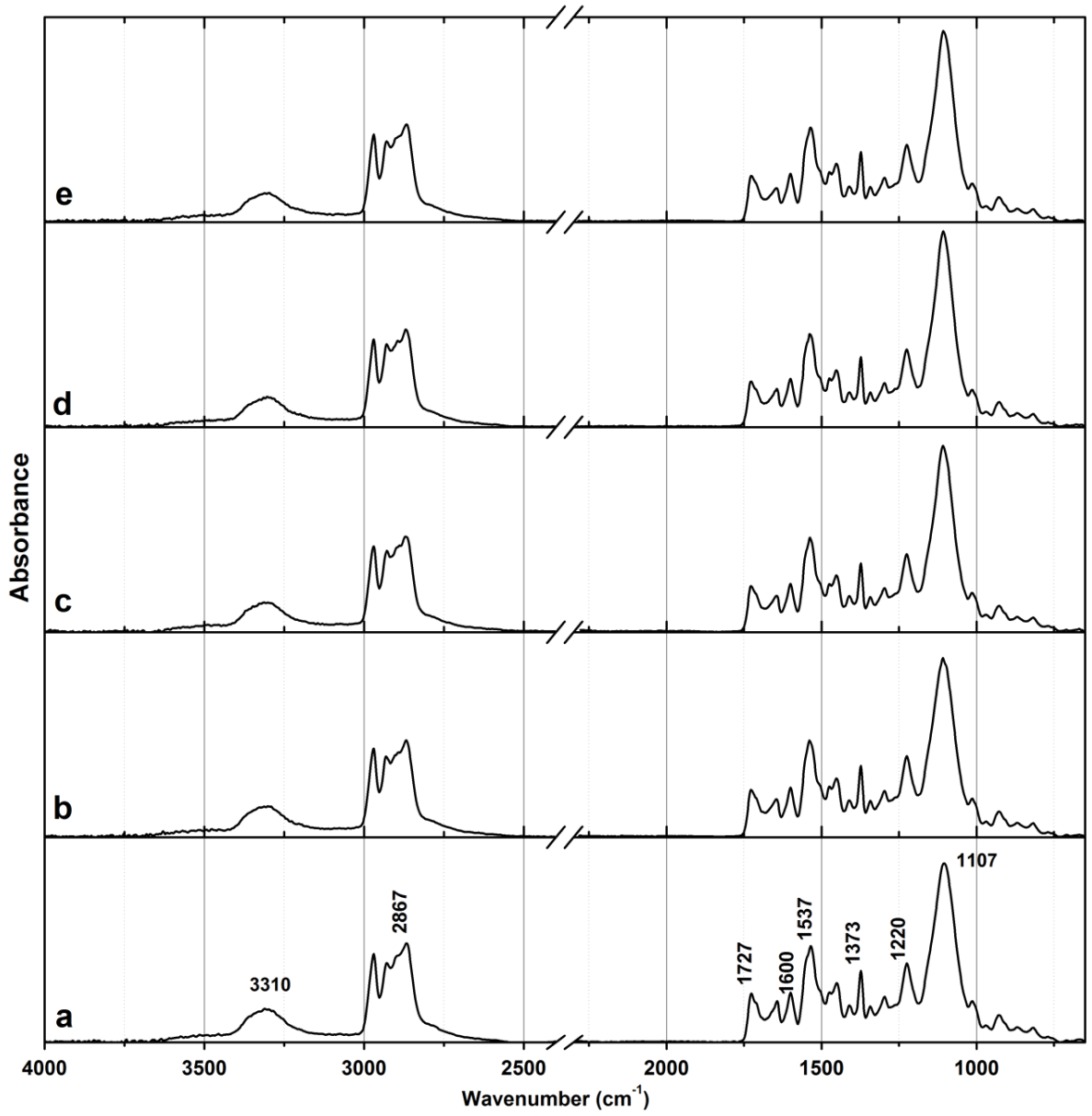


Figure VI.1 Infrared spectra of the unaged ether-based PUR foam before (a) and after twelve months (b–e) of natural ageing in the dark from 4000 to 650 cm^{-1}: anoxic storage (b), cool-enclosed storage (c), enclosed storage (d) and open-air storage (e).

VI.2 Naturally pre-aged model of ether-based PUR foam

VI.2.1 Weight variations

Weight measurements for the different exposure times are presented in Table VI.2. The values obtained are the result of three independent measurements.

Table VI.2 Weight variations (g) for the naturally pre-aged ether-based PUR foam samples during the dark ageing experiment

Storage Condition	1 month		3 months		6 months		9 months		12 months	
	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)
Open-Air	-0.00081	-0.22192	0.00156	0.44048	0.00048	0.13304	0.00126	0.35229	0.00046	0.12966
Enclosed	-0.00084	-0.23145	0.00134	0.38225	0.00065	0.17659	0.00135	0.39582	0.00057	0.16658
Cool-enclosed	-0.00004	-0.01253	0.00224	0.63424	0.00004	0.01035	-0.00037	-0.10194	-0.00006	-0.01972
Anoxic	-0.00055	-0.16325	0.00151	0.43326	-0.00037	-0.10434	-0.00061	-0.17056	-0.00011	-0.02940

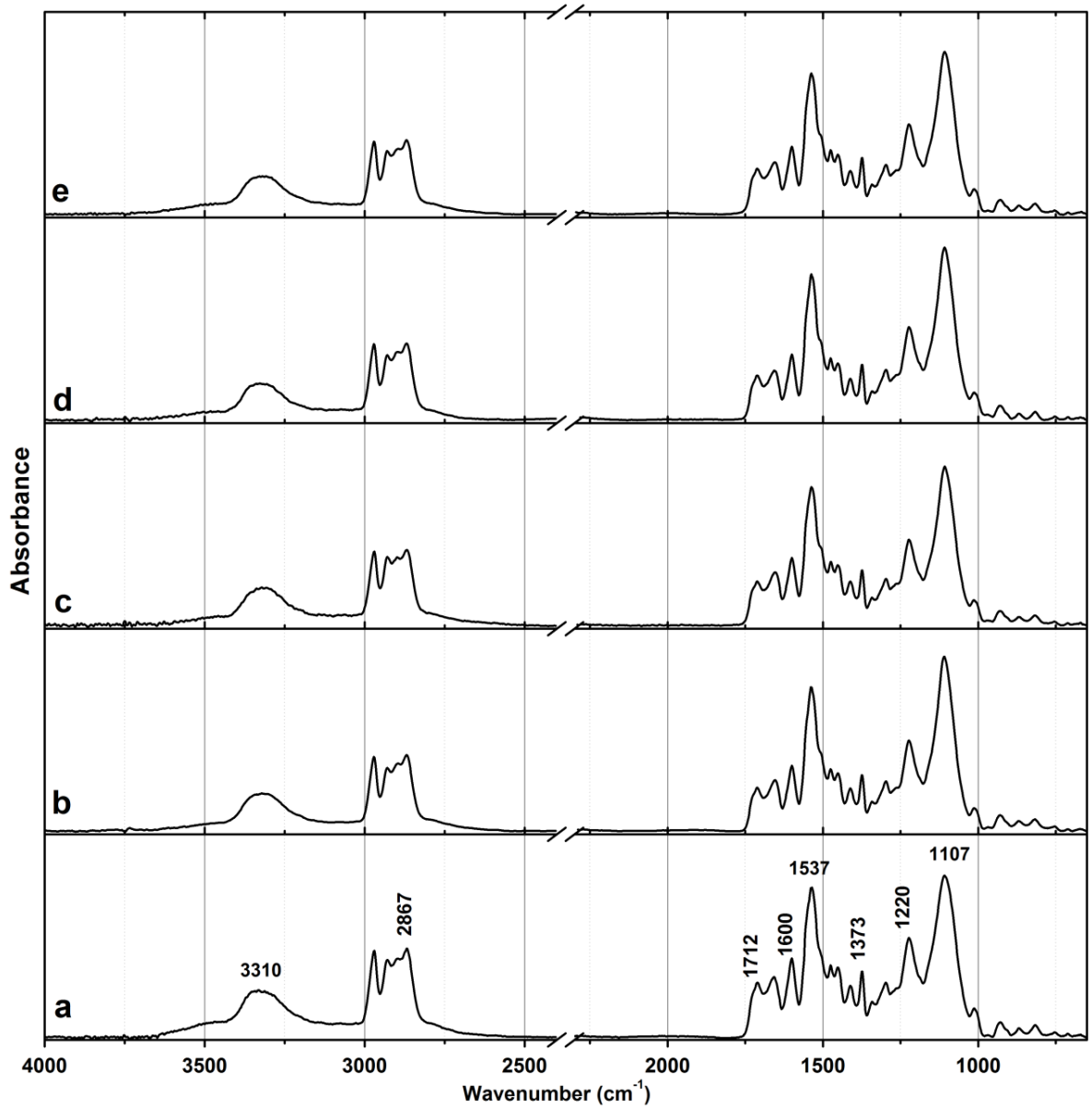


Figure VI.2 Infrared spectra of the naturally pre-aged ether-based PUR foam before (a) and after twelve months (b–e) of natural ageing in the dark from 4000 to 650 cm^{-1}: anoxic storage (b), cool-enclosed storage (c), enclosed storage (d) and open-air storage (e).

VI.3 Unaged model of ester-based PUR foam

VI.3.1 Weight variations

Weight measurements for the different exposure times are presented in Table VI.3. The values obtained are the result of three independent measurements.

Table VI.3 Weight variations (g) for the unaged ester-based PUR foam samples during the dark ageing experiment

Storage Condition	1 month		3 months		6 months		9 months		12 months	
	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)
Open-Air	-0.00191	-0.20254	0.00434	0.46659	0.00172	0.16990	0.00343	0.38422	0.00171	0.17388
Enclosed	-0.00285	-0.32119	0.00325	0.36946	0.00083	0.07667	0.00322	0.37127	0.00113	0.12294
Cool-enclosed	-0.00102	-0.10887	0.00582	0.59392	-0.00112	-0.11254	-0.00150	-0.16390	-0.00067	-0.06062
Anoxic	-0.00231	-0.25485	0.00367	0.45172	-0.00112	-0.13168	-0.00175	-0.21687	-0.00036	-0.04168

VI.3.2 Infrared µ-spectroscopy

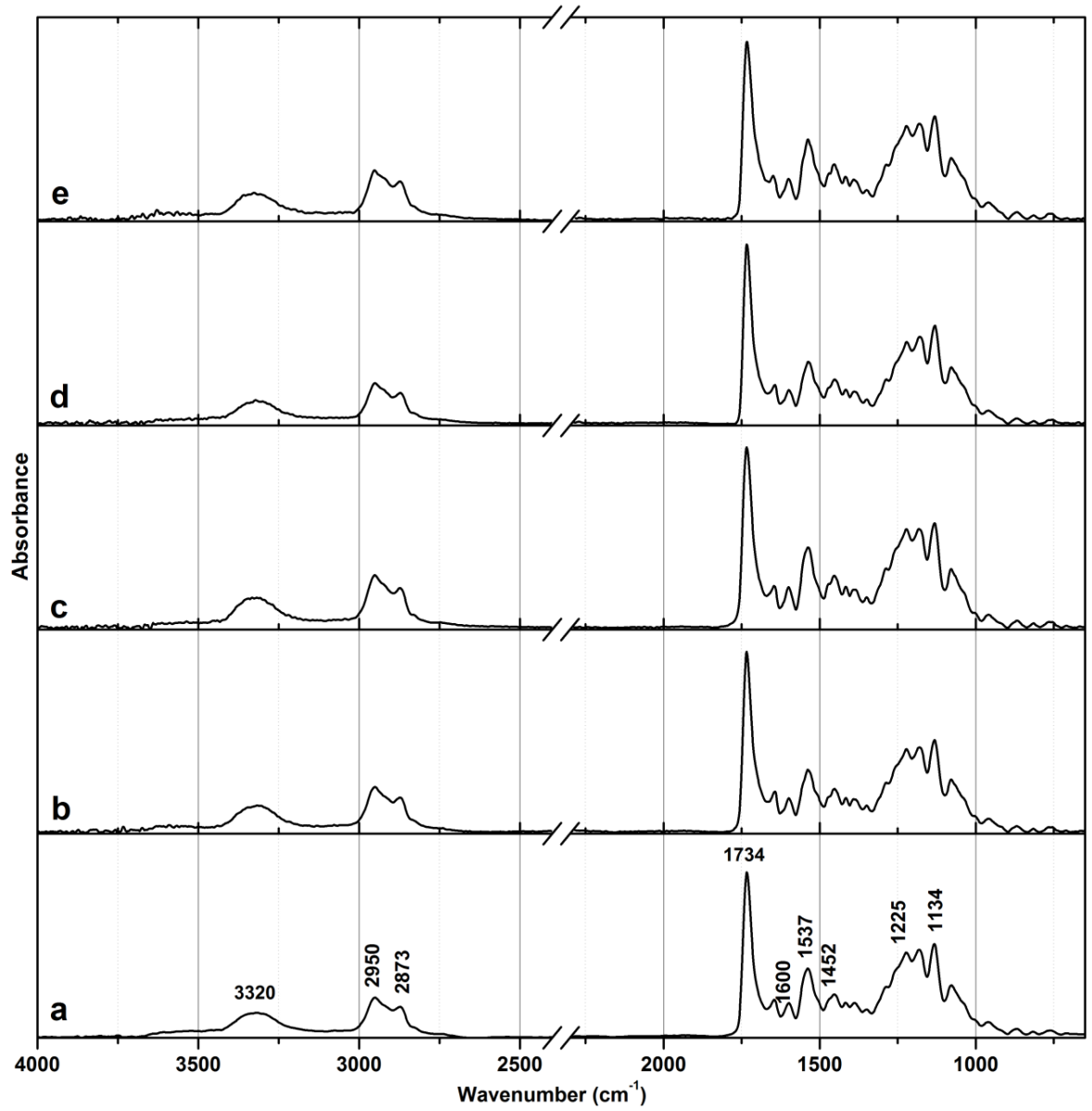


Figure VI.3 Infrared spectra of the unaged ester-based PUR foam before (a) and after twelve months (b-e) of natural ageing in the dark from 4000 to 650 cm^{-1}: anoxic storage (b), cool-enclosed storage (c), enclosed storage (d) and open-air storage (e).

VI.4 Naturally pre-aged model of ester-based PUR foam

VI.4.1 Weight variations

Weight measurements for the different exposure times are presented in Table VI.4. The values obtained are the result of three independent measurements.

Table VI.4 Weight variations (g) for the naturally pre-aged ester-based PUR foam samples during the dark ageing experiment

Storage Condition	1 month		3 months		6 months		9 months		12 months	
	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)
Open-Air	-0.00082	-0.18838	0.00196	0.45095	0.00099	0.22802	0.00176	0.38728	0.00091	0.19702
Enclosed	-0.00146	-0.33213	0.00175	0.34071	0.00048	0.09195	0.00159	0.34871	0.00051	0.11327
Cool-enclosed	-0.00047	-0.11623	0.00216	0.47040	-0.00091	-0.20640	-0.00119	-0.25218	-0.00060	-0.13937
Anoxic	-0.00064	-0.17755	0.00209	0.50388	-0.00061	-0.15216	-0.00084	-0.20005	-0.00024	-0.05168

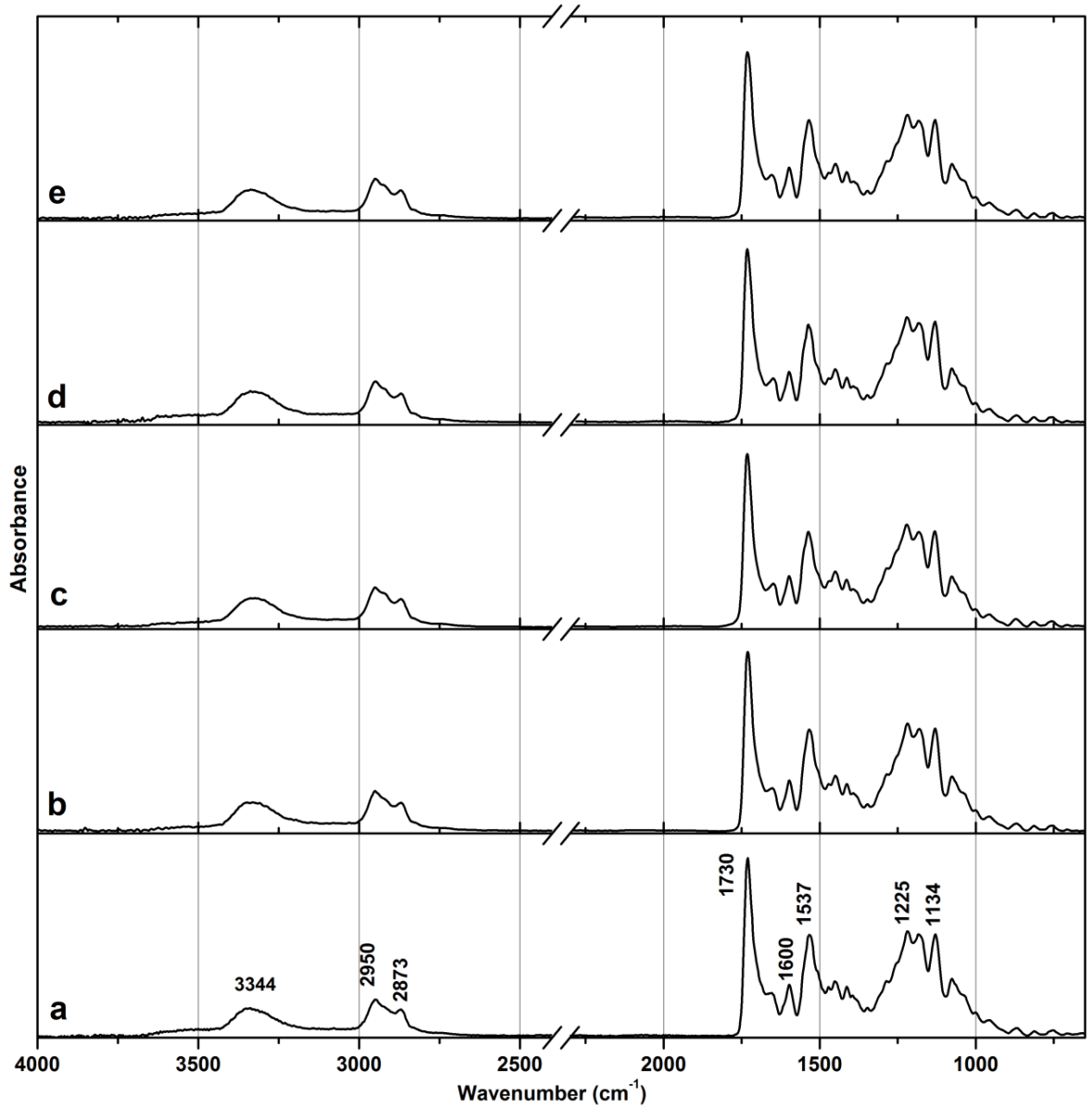


Figure VI.4 Infrared spectra of the naturally pre-aged ester-based PUR foam before (a) and after twelve months (b–e) of natural ageing in the dark from 4000 to 650 cm^{-1}: anoxic storage (b), cool-enclosed storage (c), enclosed storage (d) and open-air storage (e).

VI.5 Unaged model of ester-based TPU film

VI.5.1 Weight variations

Weight measurements for the different exposure times are presented in Table VI.5. The values obtained are the result of three independent measurements.

Table VI.5 Weight variations (g) for the unaged ester-based TPU film samples during the dark ageing experiment

Storage Condition	1 month		3 months		6 months		9 months		12 months	
	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)	Mass variation (g)	Mass variation (%)
Open-Air	-0.00007	-0.12434	0.00016	0.30151	0.00015	0.30784	0.00016	0.28406	0.00019	0.32287
Enclosed	-0.00010	-0.16952	0.00010	0.19034	0.00005	0.08115	0.00008	0.14444	0.00010	0.17548
Cool-enclosed	0.00002	0.03661	0.00028	0.40780	0.00001	0.01161	-0.00001	-0.00983	-0.00005	-0.07652
Anoxic	-0.00005	-0.08648	0.00016	0.23009	-0.00002	-0.03526	-0.00003	-0.04742	0.00002	0.02905

VI.5.2 Stereomicroscopy

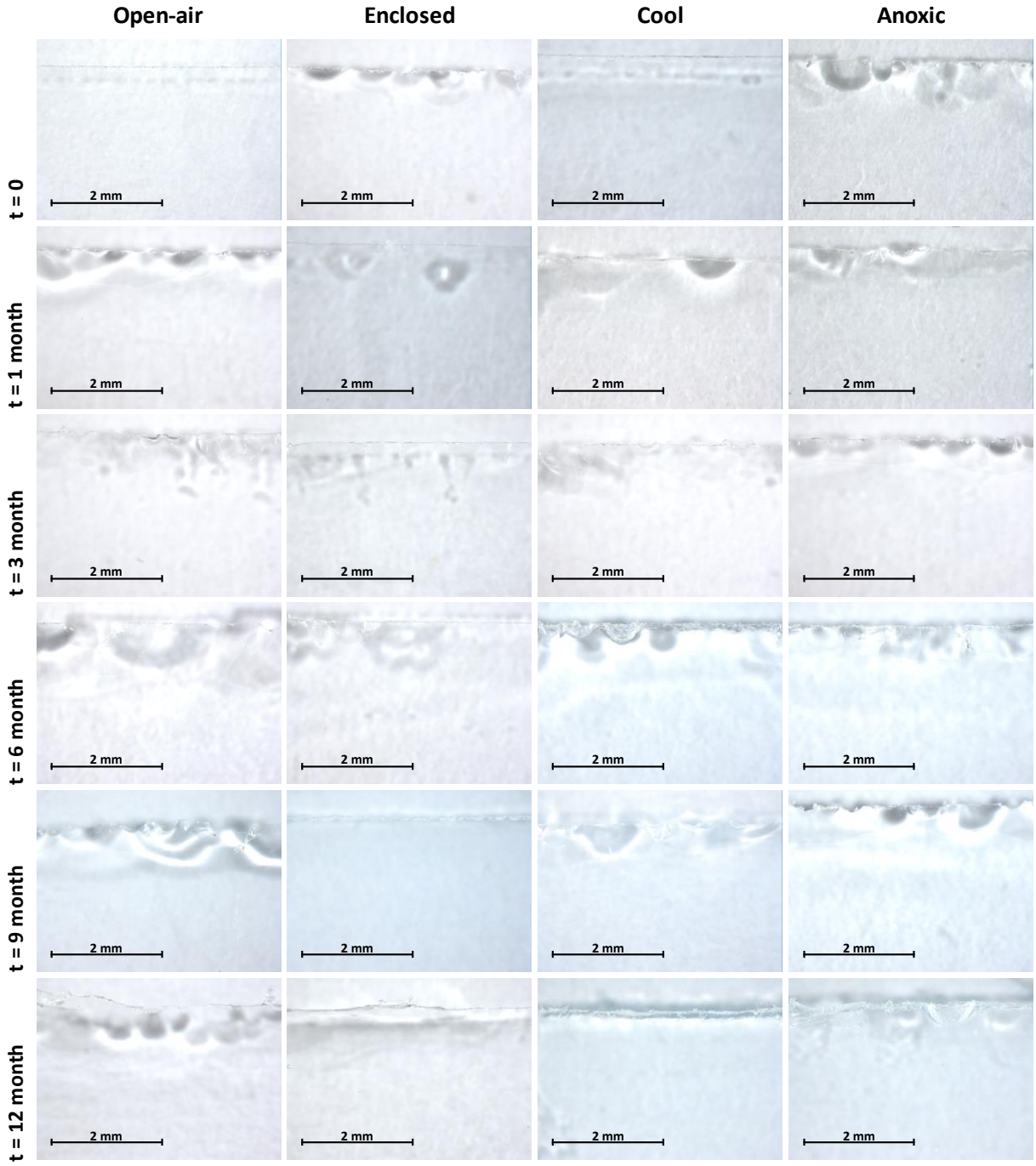


Figure VI.5 Stereomicroscopy images of the unaged ester-based TPU before (t=0) and after ageing (t=[1,12] months) in the dark in different storage conditions. Each image corresponds to a different TPU film sample.

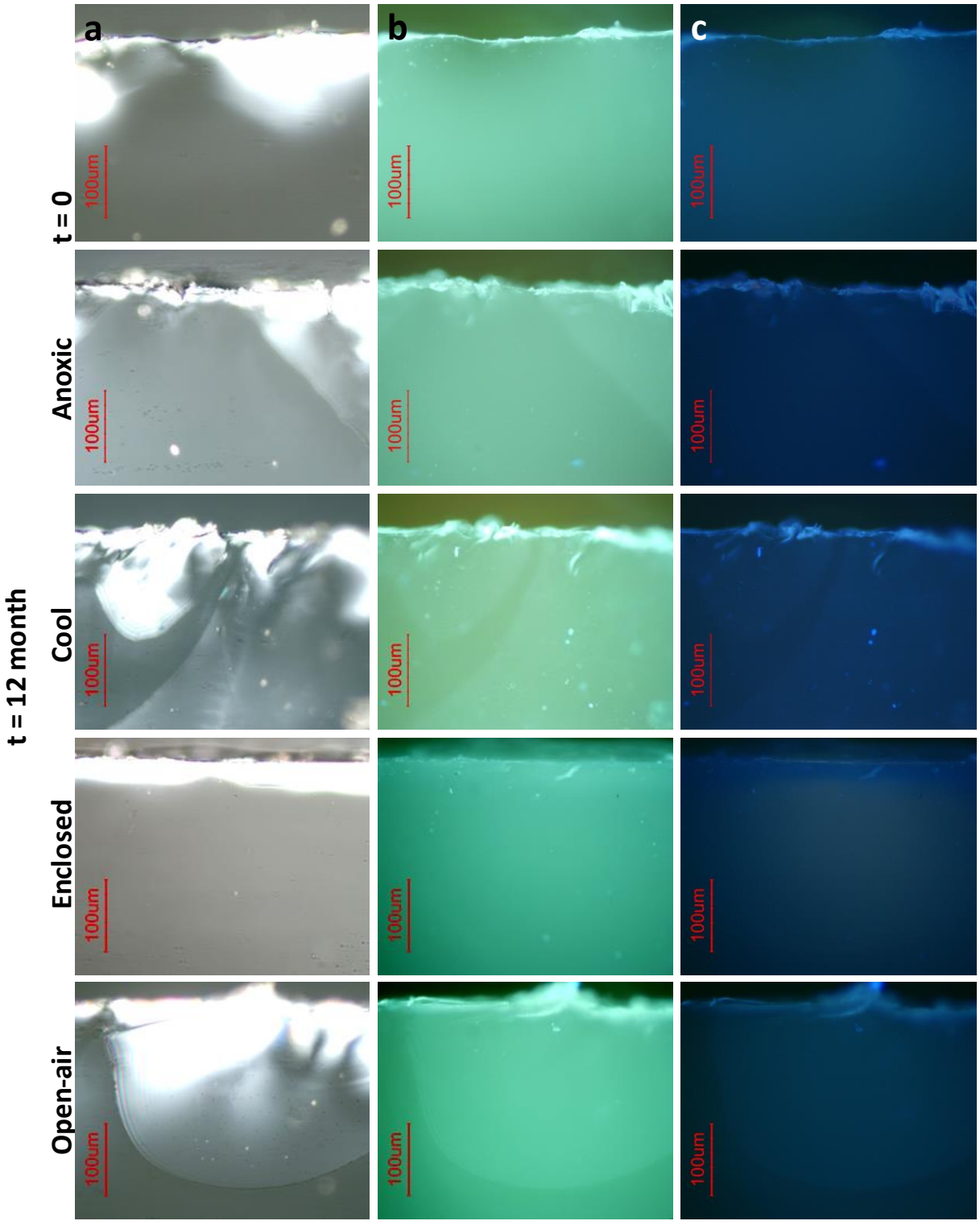


Figure VI.6 Microscopy images of the unaged ester-based TPU film before (t=0) and after (t=12 months) ageing in different storage conditions: cross-polarised light (column a), blue-violet light (column b) and ultraviolet light (column c).

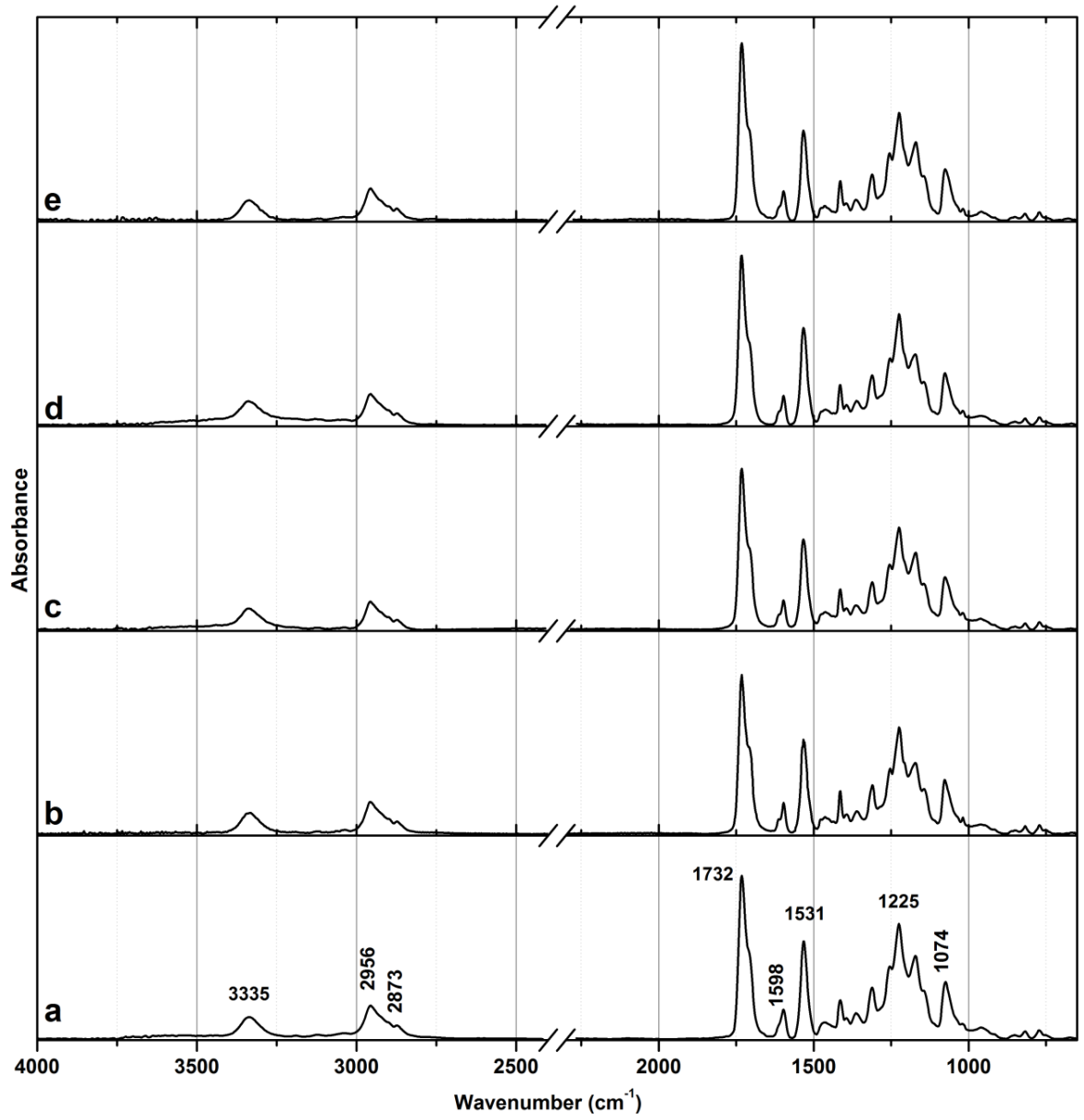


Figure VI.7 Infrared spectra of the unaged ester-based TPU film before (a) and after twelve months (b–e) of natural ageing in the dark from 4000 to 650 cm^{-1}: anoxic storage (b), cool-enclosed storage (c), enclosed storage (d) and open-air storage (e).

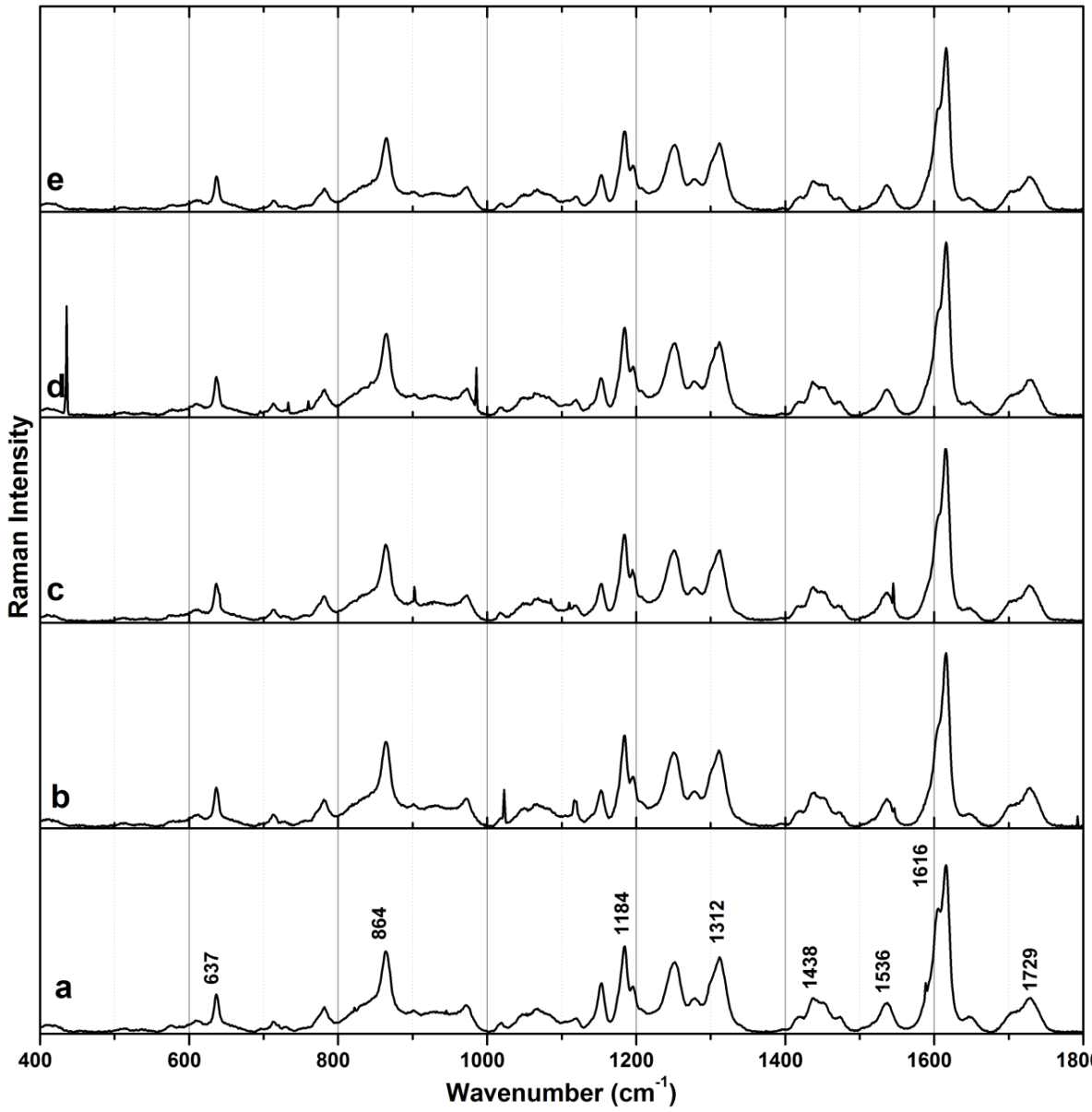


Figure VI.8 Raman spectra of the unaged ester-based TPU film before (a) and after twelve months (b–e) of natural ageing in the dark from 4000 to 650 cm^{-1}: anoxic storage (b), cool-enclosed storage (c), enclosed storage (d) and open-air storage (e).